

# The c2d *Spitzer* spectroscopic survey of ices around low-mass young stellar objects. IV. NH<sub>3</sub> and CH<sub>3</sub>OH

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## ABSTRACT

NH<sub>3</sub> and CH<sub>3</sub>OH are key molecules in astrochemical networks leading to the formation of more complex N- and O-bearing molecules, such as CH<sub>3</sub>CN and CH<sub>3</sub>OCH<sub>3</sub>. Despite a number of recent studies, little is known about their abundances in the solid state. This is particularly the case for low-mass protostars, for which only the launch of the *Spitzer* Space Telescope has permitted high sensitivity observations of the ices around these objects. In this work, we investigate the  $\sim 8 - 10 \mu\text{m}$  region in the *Spitzer* IRS (InfraRed Spectrograph) spectra of 41 low-mass young stellar objects (YSOs). These data are part of a survey of interstellar ices in a sample of low-mass YSOs studied in earlier papers in this series. We used both an empirical and a local continuum method to correct for the contribution from the  $10 \mu\text{m}$  silicate absorption in the recorded spectra. In addition, we conducted a systematic laboratory study of NH<sub>3</sub>- and CH<sub>3</sub>OH-containing ices to help interpret the astronomical spectra. We clearly detect a feature at  $\sim 9 \mu\text{m}$  in 24 low-mass YSOs. Within the uncertainty in continuum determination, we identify this feature with the NH<sub>3</sub>  $\nu_2$  umbrella mode, and derive abundances with respect to water between  $\sim 2$  and 15%. Simultaneously, we also revisited the case of CH<sub>3</sub>OH ice by studying the  $\nu_4$  C–O stretch mode of this molecule at  $\sim 9.7 \mu\text{m}$  in 16 objects, yielding abundances consistent with those derived by Boogert et al. (2008) (hereafter paper I) based on a simultaneous  $9.75$  and  $3.53 \mu\text{m}$  data analysis. Our study indicates that NH<sub>3</sub> is present primarily in H<sub>2</sub>O-rich ices, but that in some cases, such ices are insufficient to explain the observed narrow FWHM. The laboratory data point to CH<sub>3</sub>OH being in an almost pure methanol ice, or mixed mainly with CO or CO<sub>2</sub>, consistent with its formation through hydrogenation on grains. Finally, we use our derived NH<sub>3</sub> abundances in combination with previously published abundances of other solid N-bearing species to find that up to 10–20 % of nitrogen is locked up in known ices.

*Subject headings:* infrared: ISM — ISM: molecules — ISM: abundances — stars: formation — astrochemistry

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## 1. Introduction

Ammonia and methanol are among the most ubiquitous and abundant (after  $\text{H}_2$  and  $\text{CO}$ ) molecules in space. Gaseous  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  are found in a variety of environments such as infrared dark clouds, dense gas surrounding ultra-compact H II regions, massive hot cores, hot corinos, and comets. Solid  $\text{CH}_3\text{OH}$  has been observed in the ices surrounding massive YSOs (e.g. Schutte et al. 1991; Dartois et al. 1999; Gibb et al. 2004) and more recently toward low-mass protostars (Pontoppidan et al. 2003). The presence of solid  $\text{NH}_3$  has been claimed toward massive YSOs only (Lacy et al. 1998; Dartois et al. 2002; Gibb et al. 2004; Gürtler et al. 2002), with the exception of a possible detection in the low-mass object IRAS 03445+3242 (Gürtler et al. 2002). However, these detections are still controversial and ambiguous (Taban et al. 2003).

Both molecules are key participants in gas-grain chemical networks resulting in the formation of more complex N- and O-bearing molecules, such as  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{OCH}_3$  (e.g. Rodgers & Charnley 2001). Moreover, UV processing of  $\text{NH}_3$ - and  $\text{CH}_3\text{OH}$ -containing ices has been proposed as a way to produce amino-acids and other complex organic molecules (e.g., Muñoz Caro & Schutte 2003; Bernstein et al. 2002; Öberg et al. 2009). In addition, the amount of  $\text{NH}_3$  in ices has a direct impact on the content of ions such as  $\text{NH}_4^+$  and  $\text{OCN}^-$ , which form reactive intermediates in solid-state chemical networks. A better knowledge of the  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  content in interstellar ices will thus help to constrain chemical models and to gain a better understanding of the formation of more complex, prebiotic, molecules.

During the pre-stellar phase,  $\text{NH}_3$  is known to freeze out on grains (if the core remains starless long enough – Lee et al. 2004). Moreover,  $\text{CH}_3\text{OH}$  is known to have gas-phase abundances with respect to  $\text{H}_2$  in hot cores/corinos that are much larger than in cold dense clouds:  $\sim (1 - 10) \times 10^{-6}$  vs  $\leq 10^{-7}$ , with the former values most likely representing evaporated ices in warm regions (e.g. Genzel et al. 1982; Blake et al. 1987; Federman et al. 1990). Together, these findings

suggest that ices are an important reservoir of  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  and that prominent features should be seen in the absorption spectra toward high- and low-mass protostars. Unfortunately, as summarized in Table 1,  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  bands, with the exception of the  $3.53 \mu\text{m}$   $\text{CH}_3\text{OH}$  feature, are often blended with deep water and/or silicate absorptions, complicating unambiguous identifications and column density measurements. This is particularly true for  $\text{NH}_3$  whose abundance determination based on the presence of an ammonium hydrate feature at  $3.47 \mu\text{m}$  remains controversial (e.g. Dartois & d’Hendecourt 2001). Nonetheless, it is important to use all available constraints to accurately determine the abundances of these two molecules. Despite the overlap with the  $10 \mu\text{m}$  silicate (Si–O stretch) feature, the  $\text{NH}_3$   $\nu_2$  umbrella mode at  $\sim 9 \mu\text{m}$  ( $\sim 1110 \text{ cm}^{-1}$ ) offers a strong intrinsic absorption cross section and appears as the most promising feature to determine the abundance of this species in the solid phase. Moreover, the  $\text{CH}_3\text{OH}$   $\nu_4$  C–O stretch at  $\sim 9.7 \mu\text{m}$  ( $\sim 1030 \text{ cm}^{-1}$ ) provides a good check on the validity of the different methods we will use to subtract the  $10\text{-}\mu\text{m}$  silicate absorption, since the abundance of this molecule has been accurately determined previously from both the  $3.53$  and  $9.75 \mu\text{m}$  features (see Paper I).

More detailed spectroscopic information is particularly interesting for low-mass protostars as the ice composition reflects the conditions during the formation of Sun-like stars. Such detections have only become possible with *Spitzer*, whose sensitivity is necessary to observe low luminosity objects even in the nearest star-forming clouds. The spectral resolution of the *Spitzer* Infrared Spectrograph (IRS, Houck et al. 2004) of  $\Delta\lambda/\lambda \sim 100$  in this wavelength range is comparable to that of the Infrared Space Observatory (ISO) PHOT-S instrument but lower than that of the ISO-SWS and other instruments used to identify solid  $\text{NH}_3$  toward high luminosity sources. The spectral appearance of ice absorption features, such as band shape, band position and integrated band strength, is rather sensitive to the molecular environment. Thus, the interpretation of the astronomical spectra should be supported by a systematic laboratory study of interstellar ice analogues containing  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$ . Changes in the lattice geometry and physical conditions

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TABLE 1  
SELECTED NEAR- AND MID-INFRARED FEATURES OF NH<sub>3</sub> AND CH<sub>3</sub>OH.

Mode	$\lambda$ ( $\mu\text{m}$ )	$\bar{\nu}$ ( $\text{cm}^{-1}$ )	Problem
NH <sub>3</sub> features:			
$\nu_3$ N–H stretch	2.96	3375	Blended with H <sub>2</sub> O (O–H stretch, 3.05 $\mu\text{m}$ /3275 $\text{cm}^{-1}$ )
$\nu_4$ H–N–H bend	6.16	1624	Blended with H <sub>2</sub> O (H–O–H bend, 5.99 $\mu\text{m}$ /1670 $\text{cm}^{-1}$ ), HCOOH
<b><math>\nu_2</math> umbrella</b>	<b>9.00</b>	<b>1110</b>	<b>Blended with silicate</b>
CH <sub>3</sub> OH features:			
$\nu_2$ C–H stretch	3.53	2827	–
$\nu_6$ & $\nu_3$ –CH <sub>3</sub> deformation	6.85	1460	Blended (e.g. with NH <sub>4</sub> <sup>+</sup> )
$\nu_7$ –CH <sub>3</sub> rock	8.87	1128	Weak; blended with silicate
<b><math>\nu_4</math> C–O stretch</b>	<b>9.75</b>	<b>1026</b>	<b>Blended with silicate</b>
Torsion	14.39	695	Blended with H <sub>2</sub> O libration mode

NOTE.—The bold-faced lines indicate the features studied here.

NOTE.—The nomenclature for the NH<sub>3</sub> and CH<sub>3</sub>OH vibrational modes are adopted from Herzberg (1945).

of an ice are directly reflected by variations in these spectral properties. In the laboratory, it is possible to record dependencies over a wide range of astrophysically relevant parameters, most obviously ice composition, mixing ratios, and temperature. Such laboratory data exist for pure and some  $\text{H}_2\text{O}$ -rich  $\text{NH}_3$ - and  $\text{CH}_3\text{OH}$ -containing ices (e.g., d’Hendecourt & Allamandola 1986; Hudgins et al. 1993; Kerkhof et al. 1999; Taban et al. 2003), but a systematic study and comparison with observational spectra is lacking.

In principle, the molecular environment also provides information on the formation pathway of the molecule. For example,  $\text{NH}_3$  ice is expected to form simultaneously with  $\text{H}_2\text{O}$  and  $\text{CH}_4$  ice in the early, low-density molecular cloud phase from hydrogenation of N atoms (e.g., Tielens & Hagen 1982). In contrast, solid  $\text{CH}_3\text{OH}$  is thought to result primarily from hydrogenation of solid CO, a process which has been confirmed to be rapid at low temperatures in several laboratory experiments (e.g. Watanabe & Kouchi 2002; Hidaka et al. 2004; Fuchs et al. 2009). A separate, water-poor layer of CO ice is often found on top of the water-rich ice layer in low-mass star-forming regions due to the ‘catastrophic’ freeze-out of gas-phase CO at high densities (Pontoppidan et al. 2003; Pontoppidan 2006). Hydrogenation of this CO layer should lead to a nearly pure  $\text{CH}_3\text{OH}$  ice layer (e.g., Cuppen et al. 2009), which will have a different spectroscopic signature from that of  $\text{CH}_3\text{OH}$  embedded in a water-rich matrix. The latter signature would be expected if  $\text{CH}_3\text{OH}$  ice were formed by hydrogenation of CO in a water-rich environment or by photoprocessing of  $\text{H}_2\text{O}:\text{CO}$  ice mixtures, another proposed route (e.g., Moore & Hudson 1998).

Here, we present *Spitzer* spectra between 5 and 35  $\mu\text{m}$  of ices surrounding 41 low-mass protostars, focusing on the  $\sim 8 - 10 \mu\text{m}$  region that contains the  $\nu_2$  umbrella and  $\nu_4$  C–O stretch modes of  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$ , respectively. This work is the fourth paper in a series of ice studies (Boogert et al. 2008; Pontoppidan et al. 2008; Öberg et al. 2008) carried out in the context of the *Spitzer* Legacy Program “From Molecular Cores to Planet-Forming Disks” (“c2d”; Evans et al. 2003). In Section 2, we carry out the analysis of the *Spitzer* data in 8–10  $\mu\text{m}$  range. In Section 3, we present the laboratory data specifically obtained to help interpret

the data that are discussed in Section 4. Finally, we conclude in Section 5 with a short discussion of the joint astronomy-laboratory work (including the overall continuum determination).

## 2. Astronomical observations and analysis

The source sample consists of 41 low-mass YSOs that were selected based on the presence of ice absorption features. The entire sample spans a wide range of spectral indices  $\alpha = -0.25$  to  $+2.70$ , with  $\alpha$  defined as  $d \log(\lambda F_\lambda) / d \log(\lambda)$ , where  $d$  indicates the derivative, and  $F_\lambda$  represents all the photometric fluxes available between  $\lambda = 2.17 \mu\text{m}$  (2MASS  $K_s$ -band) and  $\lambda = 24 \mu\text{m}$  (*Spitzer*/MIPS band). In the infrared broad-band classification scheme, 35 out of 41 objects fall in the embedded Class 0/I category ( $\alpha > 0.3$ ). The remaining 6 objects are flat-spectrum type objects ( $-0.3 < \alpha < 0.3$ ; Greene et al. 1994).

*Spitzer*/IRS spectra (5–35  $\mu\text{m}$ ) were obtained as part of the c2d Legacy program (PIDs 172 and 179), as well as a dedicated open time program (PID 20604), and several previously published GTO spectra (Watson et al. 2004). We refer the reader to Table 1 and Section 3 of Boogert et al. (2008) for the source coordinates and a description of the data reduction process (including overall continuum determination).

As mentioned previously, spectral signatures in the  $\sim 8 - 10 \mu\text{m}$  region are dominated by the Si–O stretching mode of silicates. The overall shape as well as the sub-structure of the silicate feature depend on grain size, mineralogy, level of crystallinity. These effects are degenerate and so these different factors cannot be easily separated. For example, large grains and the presence of SiC both produce a shoulder at 11.2  $\mu\text{m}$  (e.g., Min et al. 2007). Therefore, trying to fit the 10  $\mu\text{m}$  silicate feature by determining the composition and size of the grains is a complex process. For this reason, we use two alternative methods to model the silicate profile and extract the  $\text{NH}_3$  (and  $\text{CH}_3\text{OH}$ ) feature(s) from the underlying silicate absorption.

### 2.1. Local continuum

The first method uses a local continuum to fit the shape of the silicate absorption. For this, we fit a fourth order polynomial over the wavelength

ranges 8.25–8.75, 9.23–9.37, and 9.98–10.4  $\mu\text{m}$ , avoiding the positions where  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  absorb around 9 and 9.7  $\mu\text{m}$ . These fits are shown with thick black lines in Fig. 1. After subtraction of the local continuum from the observations, we fit a Gaussian to the remaining  $\text{NH}_3$  and/or  $\text{CH}_3\text{OH}$  feature, when present, as shown in Fig. 2. The results of the Gaussian fits are listed in Table A.1 of Appendix A.

## 2.2. Template

The second method assumes that the 8–10  $\mu\text{m}$  continuum can be represented by a template silicate absorption feature, selected among the observed sources. A comparison of the results obtained using a template to those obtained using a simple local continuum provides an estimate of the influence of the continuum choice on the shape and depth of the  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  features. The templates were chosen using an empirical method. Upon examination of the 10  $\mu\text{m}$  feature of the entire sample, the sources could be separated into three general categories, depending on the shape of the wing of the silicate absorption between  $\sim 8$  and 8.7  $\mu\text{m}$  (which we will refer to as the 8  $\mu\text{m}$  wing): (i) sources with a straight 8  $\mu\text{m}$  wing (Fig. 3-a), (ii) sources with a curved 8  $\mu\text{m}$  wing (Fig. 3-b), and (iii) sources with a rising 8  $\mu\text{m}$  wing (“emission” sources, Fig. 3-c).

Note that, since radiative transfer in the 8–10  $\mu\text{m}$  region can be complicated by the presence of silicate emission, we only consider sources that are the least affected by emission, that is those falling in one of the first two categories. Nevertheless, non-rising silicate profiles might still suffer from the presence of emission. To try and estimate the impact of this potential effect, we used two silicate emission sources from Kessler-Silacci et al. (2006), and subtracted these emission profiles from our absorption profiles, assuming that the emission represented 10 to 50% of the observed absorption. After removal of a local continuum, we determined the integrated optical depths of the  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  features in the spectra corrected for emission, and compared these to the integrated optical depths of the uncorrected spectra. We find that the difference can be up to a factor of two and therefore identify this possible presence of underlying emission as the largest source of uncertainty in our abundance determinations.

For each of the straight and curved 8  $\mu\text{m}$  wings, two sources (in order to test for template-dependent effects) were selected as possible templates for the silicate feature. The selection criteria were: (i) a silicate feature as deep as possible to minimize the effects of silicate emission and (ii) little  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  signal, as estimated after subtraction of a local continuum. Additionally, we added to this list the GCS3 spectrum observed by Kemper et al. (2004) toward the Galactic Center. The spectra of these templates in the 8–10  $\mu\text{m}$  region are displayed in Fig. 4.

For all the other sources in our sample, the best template was determined by scaling the possible templates to the observed optical depth at different wavelengths (8.75, 9.30, 9.37, 9.70, 9.98  $\mu\text{m}$ ) and finding the combination (template+scaling point) that gave the least residuals over the same wavelength ranges used to estimate the local continuum (8.25–8.75, 9.23–9.37, 9.98–10.4  $\mu\text{m}$ ). The result of this process is displayed for each source in the top part of Fig. 1, where the best template is shown by a grey line. The bottom panels of Fig. 1 show sources for which no reasonable template could be found, as well as emission sources, in which case only the local continuum is overlaid. As in the case of the local continuum method, the spectra obtained after subtraction of the templates are shown in Fig. 2. Taken together,  $\text{NH}_3$  features are detected in 24 out of 41 sources.

The top panel of Figure 2 shows that the  $\text{CH}_3\text{OH}$  feature is not affected by the continuum choice, whereas the width of the  $\text{NH}_3$  band is somewhat sensitive to this choice, especially if there is no  $\text{CH}_3\text{OH}$  absorption, in which case the local continuum yields a wider  $\text{NH}_3$  profile. For both continua, there is a clear feature around 9  $\mu\text{m}$ , which we attribute to  $\text{NH}_3$ , with the characteristics and limitations given and discussed in the following sections.

## 2.3. $\text{NH}_3$ ice column densities and abundances

Gaussian fits were performed to the  $\text{NH}_3$  and/or  $\text{CH}_3\text{OH}$  features when present, and derived parameters for  $\text{NH}_3$  are listed in Table A.1 (Appendix A). Table 2 gives the column densities derived for  $\text{NH}_3$  for each of the two methods employed to determine the continuum, using a band strength of  $1.3 \times 10^{-17}$  cm molecule $^{-1}$

for the  $\text{NH}_3$   $\nu_2$  umbrella mode appropriate for a water-rich ice (d'Hendecourt & Allamandola 1986; Kerkhof et al. 1999). The two methods generally agree to within a factor of 2 or better. A similar factor of  $\leq 2$  overall uncertainty is estimated for those sources for which only the local continuum has been used.

The position of the  $\text{NH}_3$   $\nu_2$  umbrella mode is very close to that of the  $\nu_7$   $\text{CH}_3$ -rock mode of  $\text{CH}_3\text{OH}$ . As illustrated by our laboratory data (see Section 3), sources with an absorption depth at  $\sim 9.7$   $\mu\text{m}$  (CO-stretch mode of  $\text{CH}_3\text{OH}$ ) at least twice as large as the absorption depth at  $\sim 9$   $\mu\text{m}$  (blend of  $\text{CH}_3$ -rock mode of  $\text{CH}_3\text{OH}$  and  $\text{NH}_3$  umbrella mode) have a significant contribution to the 9- $\mu\text{m}$  integrated optical depth from the  $\text{CH}_3$ -rock mode of  $\text{CH}_3\text{OH}$ . In these cases (sources followed by an asterisk in Table 2 and in Table A.1 of Appendix A), we performed the following correction: we scaled a  $\text{H}_2\text{O}:\text{CH}_3\text{OH}=9:1$  laboratory spectrum to the observed optical depth of the CO-stretch mode of  $\text{CH}_3\text{OH}$ , determined the integrated optical depth of the  $\text{CH}_3$ -rock mode of  $\text{CH}_3\text{OH}$  in that scaled spectrum, and subtracted it from the total observed optical depth at 9  $\mu\text{m}$ . This correction is justified by the fact that the  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3=10:4:1$  spectrum, a typical interstellar abundance mixture, is well reproduced around 8–10  $\mu\text{m}$  by a combination of  $\text{H}_2\text{O}:\text{CH}_3\text{OH}=9:1$  and  $\text{H}_2\text{O}:\text{NH}_3=9:1$  (see Sec. 3).

The inferred  $\text{NH}_3$  ice abundances range from  $\lesssim 1\%$  to 15% with respect to  $\text{H}_2\text{O}$  ice, excluding the abnormally high value of EC 82. When considering all values (except that of EC 82) determined with the local continuum method, this relative abundance is centered on 5.3% with a standard deviation of 2.0%. If we use values determined with the template method whenever available, we find a mean of  $7.0 \pm 3.2\%$ . Either way, within the errors, this is similar to what was obtained by Öberg et al. (2008) for  $\text{CH}_4$  ( $4.7 \pm 1.6\%$ ), another ice component that should form via hydrogenation. For 6 out of the 8 sources where both  $\text{NH}_3$  and  $\text{CH}_4$  are detected, the  $\text{NH}_3$ -to- $\text{CH}_4$  abundance ratio is slightly larger than 1 ( $\sim 1.2$ ). Based on elemental abundance ratios, one would expect  $\text{NH}_3/\text{CH}_4$  smaller than 1, but since two thirds of the carbon is in refractory grains and some fraction of the gaseous CO locked up in CO at the ice formation threshold,  $\text{NH}_3$ -to- $\text{CH}_4$  ratios larger

than 1 are consistent with both  $\text{NH}_3$  and  $\text{CH}_4$  being formed by hydrogenation of N and C, respectively. Further comparison between these and other ice species will be addressed in an upcoming paper (Öberg et al. in preparation).

Regarding  $\text{CH}_3\text{OH}$ , we only report values for the Gaussian parameters and derived column densities in the appendix (see Table A.2), to show that the numbers we obtain in this independent study are consistent with those reported in Paper I. Our recommended abundances are those from paper I, based on the combined 9.75 and 3.53  $\mu\text{m}$  analysis. The inferred  $\text{CH}_3\text{OH}$  abundances range from  $< 1\%$  to  $> 25\%$  with respect to  $\text{H}_2\text{O}$  ice, indicating significant  $\text{CH}_3\text{OH}/\text{NH}_3$  abundance variations from source-to-source. Such relative abundance variations can already be clearly seen from the changing relative depths of the 9.0 and 9.7  $\mu\text{m}$  features (see also Paper I). Thus,  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  ice are likely formed through different formation pathways and/or in different ice environments.

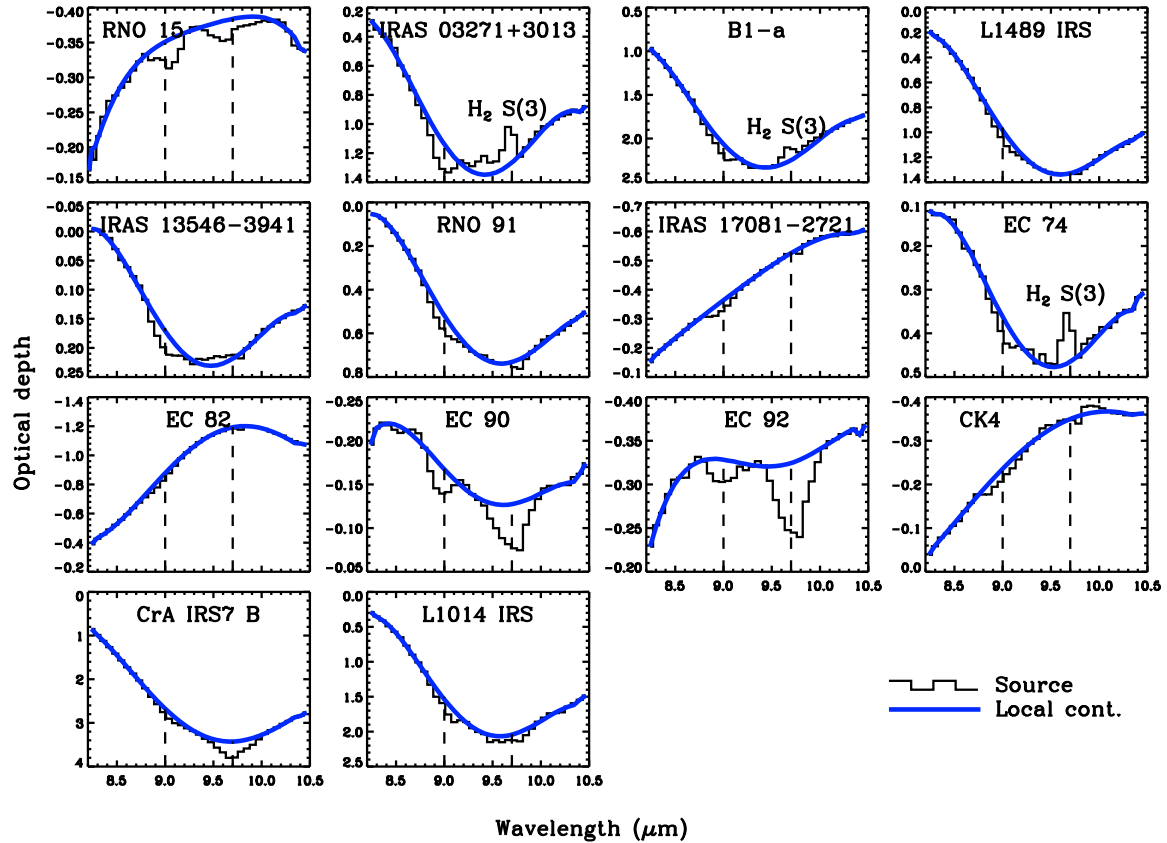
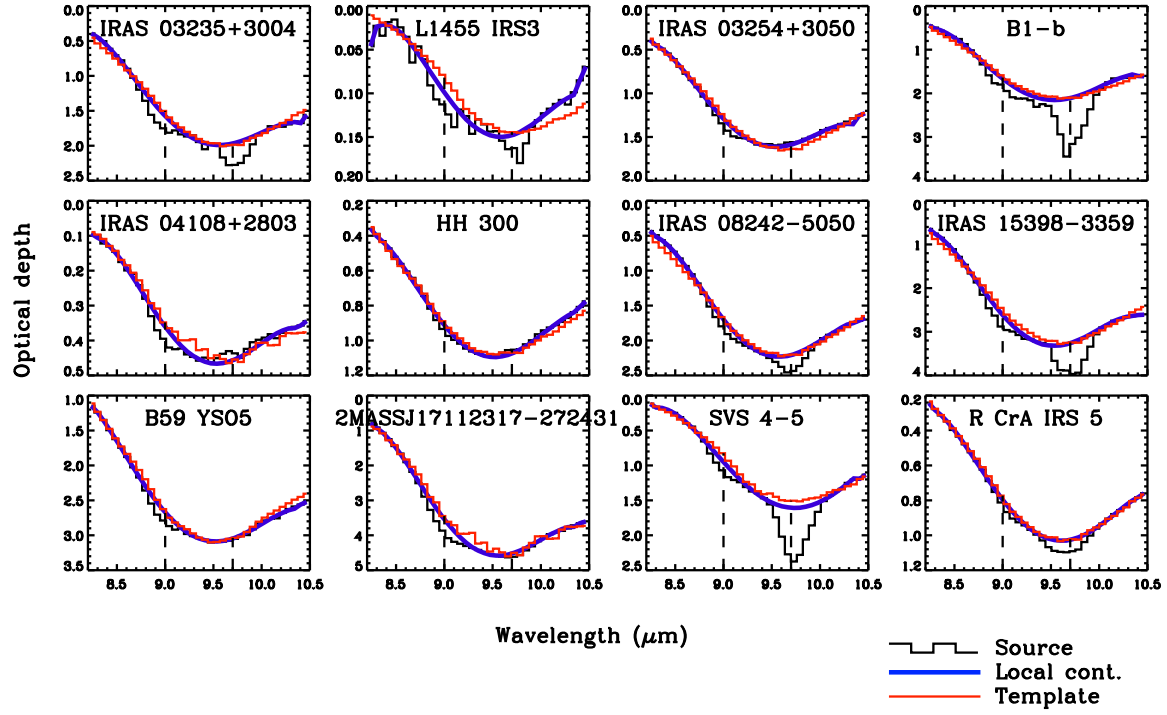


Fig. 1.— (Top) Local continuum (thick blue/black lines) and template (red/grey lines) fits to all sources for which a template could be found. (See Section 2.2 for details) — (Bottom) Local continuum fits to emission sources or sources for which no reasonable template could be found.

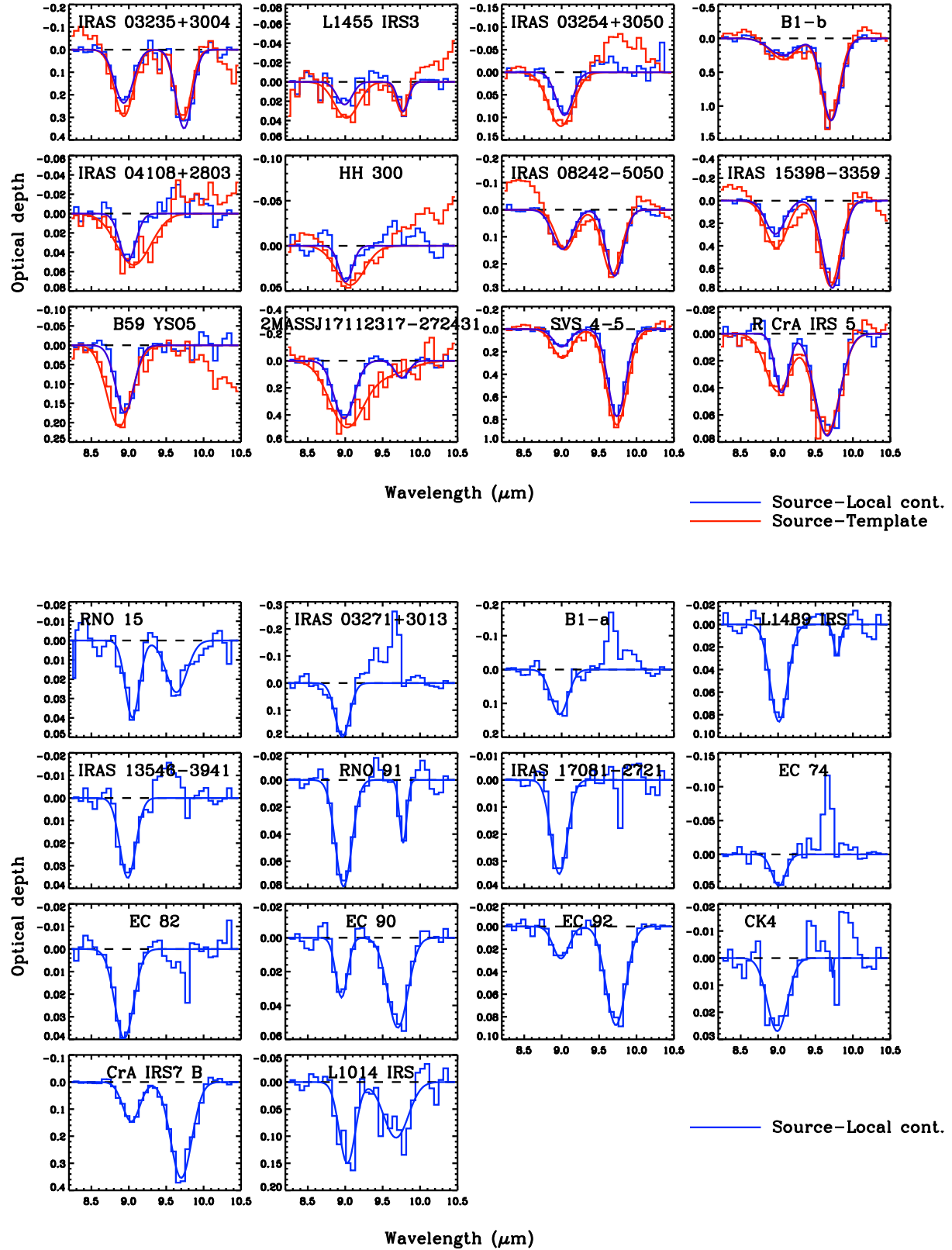


Fig. 2.— (Top) Residual after removal of local continuum and template fits for all sources for which a template could be found. (See Section 2.2 for details) — (Bottom) Residual after removal of local continuum fits for emission sources or sources for which no reasonable template could be found.



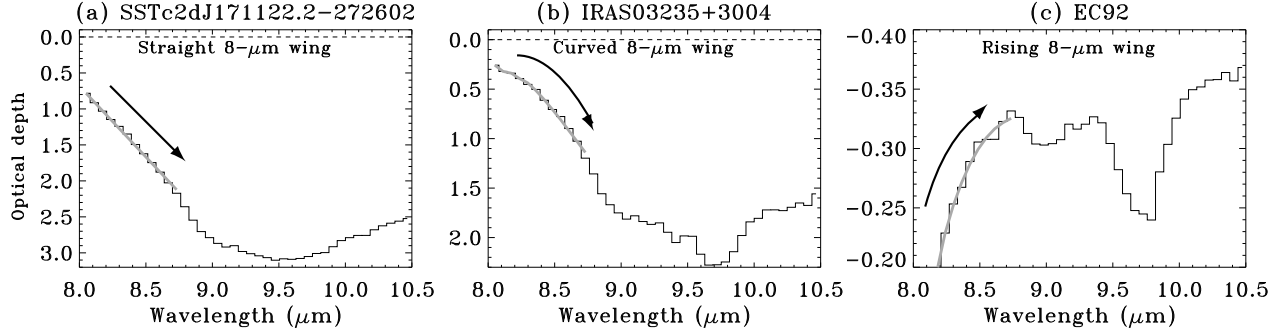


Fig. 3.— Examples illustrating the three shapes of the 8  $\mu$ m wing shown by the thick grey line: (a) straight, (b) curved, and (c) rising.

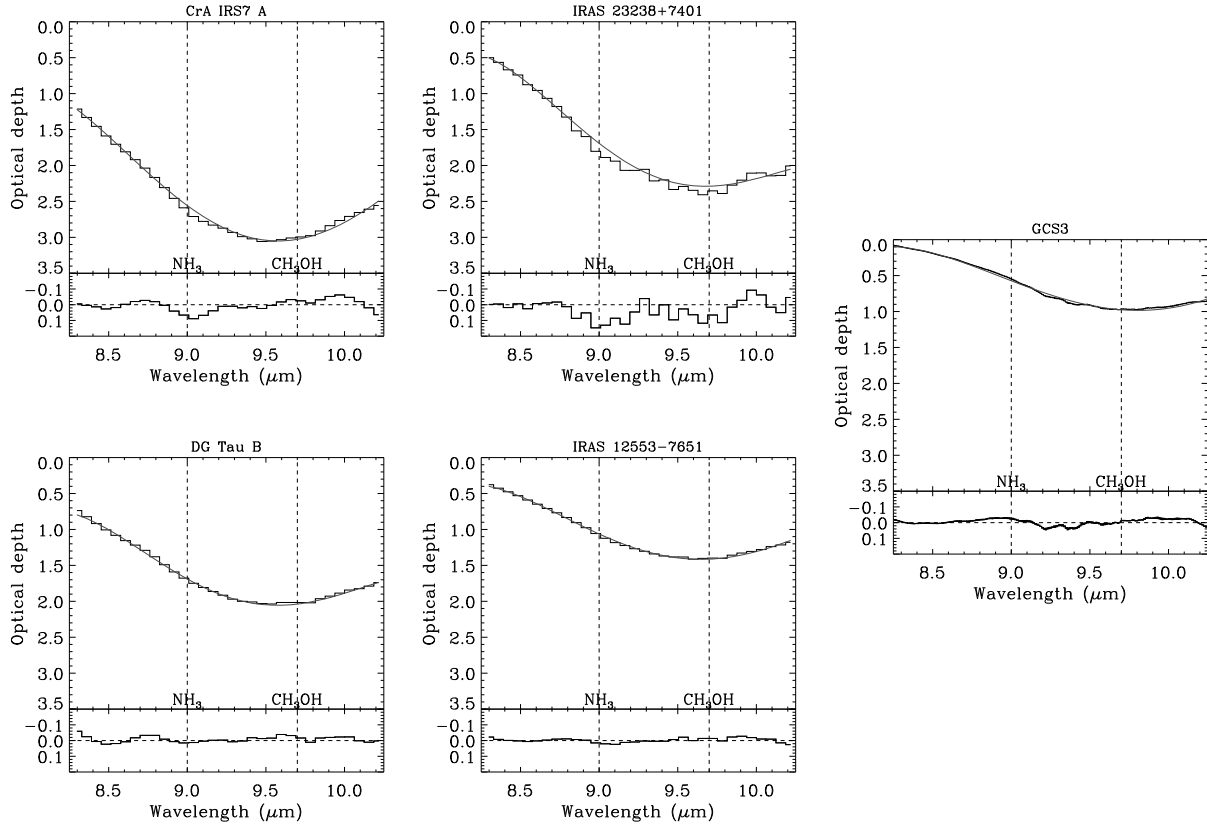


Fig. 4.— Silicate features of the sources used as templates for a straight 8  $\mu$ m wing (left), curved 8- $\mu$ m wing (middle), and GCS3 (right). The bottom panels of each plot are the residuals after removal of the local continuum shown in grey in the top panels. The optical depth scale is kept fixed for comparison. These sources are selected to have no or at most weak  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  absorptions.

TABLE 2  
NH<sub>3</sub> COLUMN DENSITIES<sup>a</sup> AND ABUNDANCES WITH RESPECT TO H<sub>2</sub>O ICE<sup>b</sup>

Source	NH <sub>3</sub> , local		NH <sub>3</sub> , template		Template	Scaling point $\mu\text{m}$
	$\times 10^{17} \text{ cm}^{-2}$	% H <sub>2</sub> O <sup>b</sup>	$\times 10^{17} \text{ cm}^{-2}$	% H <sub>2</sub> O <sup>b</sup>		
IRAS 03235+3004	6.83 ( 0.98)	4.71 ( 1.00)	8.94 ( 1.03)	6.17 ( 1.20)	IRAS 12553	9.30
L1455 IRS3	0.57 ( 0.23)	6.21 ( 3.51)	1.41 ( 0.27)	15.37 ( 6.86)	GCS3	9.37
IRAS 03254+3050	2.44 ( 0.39)	6.66 ( 1.37)	4.58 ( 0.49)	12.52 ( 2.10)	IRAS 12553	10.40
B1-b*	$\sim 7.3$	$\sim 4.2$	$\sim 9.8$	$\sim 5.6$	IRAS 12553	9.70
IRAS 04108+2803	1.23 ( 0.24)	4.29 ( 1.03)	2.07 ( 0.39)	7.21 ( 1.69)	IRAS 23238	9.70
HH 300	0.90 ( 0.22)	3.46 ( 0.90)	2.23 ( 0.37)	8.60 ( 1.65)	DG Tau B	9.70
IRAS 08242-5050	4.77 ( 0.46)	6.13 ( 0.85)	4.41 ( 0.54)	5.66 ( 0.89)	IRAS 12553	9.70
IRAS 15398-3359	8.73 ( 1.18)	5.90 ( 1.77)	13.80 ( 1.35)	9.33 ( 2.65)	IRAS 12553	9.70
B59 YSO5	4.92 ( 0.72)	3.53 ( 0.88)	6.37 ( 0.99)	4.57 ( 1.17)	CrA IRS7 A	9.70
2MASSJ17112317-272431	13.10 ( 1.06)	6.70 ( 0.54)	20.60 ( 2.76)	10.58 ( 1.42)	IRAS 23238	9.70
SVS 4-5*	$\sim 2.4$	$\sim 4.3$	$\sim 5.8$	$\sim 10.3$	GCS3	8.75
R CrA IRS 5	0.91 ( 0.23)	2.54 ( 0.67)	1.49 ( 0.31)	4.15 ( 0.92)	IRAS 12553	9.70
RNO 15 <sup>c</sup>	0.80 ( 0.21)	11.58 ( 3.18)	—	—	—	—
IRAS 03271+3013	4.90 ( 0.88)	6.37 ( 1.86)	—	—	—	—
B1-a	3.46 ( 0.69)	3.33 ( 0.98)	—	—	—	—
L1489 IRS	2.31 ( 0.30)	5.42 ( 0.96)	—	—	—	—
IRAS 13546-3941	0.94 ( 0.16)	4.56 ( 0.87)	—	—	—	—
RNO 91	2.03 ( 0.30)	4.78 ( 0.81)	—	—	—	—
IRAS 17081-2721	0.86 ( 0.16)	6.54 ( 1.39)	—	—	—	—
EC 74 <sup>c</sup>	1.00 ( 0.29)	9.35 ( 3.13)	—	—	—	—
EC 82	1.22 ( 0.14)	31.31 ( 6.65)	—	—	—	—
EC 90	0.67 ( 0.20)	3.94 ( 1.24)	—	—	—	—
EC 92*	$\sim 0.5$	$\sim 3.0$	—	—	—	—
CrA IRS7 B*	$\sim 3.0$	$\sim 2.8$	—	—	—	—
L1014 IRS	3.72 ( 0.91)	5.20 ( 1.43)	—	—	—	—
CK4	0.84 ( 0.13)	5.37 ( 0.86)	—	—	—	—
<b>3-<math>\sigma</math> upper limits</b>						
LDN 1448 IRS1	0.20	4.15	—	—	—	—
IRAS 03245+3002	17.28	4.40	—	—	—	—
L1455 SMM1	15.10	8.29	—	—	—	—
IRAS 03301+3111	0.24	5.93	—	—	—	—
B1-c	11.93	4.04	—	—	—	—
IRAS 03439+3233	0.31	3.10	—	—	—	—
IRAS 03445+3242	0.47	2.09	—	—	—	—
<b>DG Tau B</b>	0.47	2.05	—	—	—	—
<b>IRAS 12553-7651</b>	0.61	2.04	—	—	—	—
Elias 29	0.28	0.93	—	—	—	—
CRBR 2422.8-342	0.52	1.23	—	—	—	—
HH 100 IRS	0.46	1.89	—	—	—	—
<b>CrA IRS7 A</b>	0.97	0.89	—	—	—	—
CrA IRAS32	5.44	10.35	—	—	—	—
<b>IRAS 23238+7401</b>	1.60	1.24	—	—	—	—

NOTE.—Sources in bold were used as templates. Uncertainties quoted in parenthesis are statistical errors from the Gaussian fits while absolute errors are up to a factor of 2.

<sup>a</sup>Derived using a bandstrength of  $1.3 \times 10^{-17} \text{ cm molecule}^{-1}$ .

<sup>b</sup>Using the H<sub>2</sub>O ice column densities listed in Paper I.

<sup>c</sup>Values are likely upper limits (see Section 4.2 for details).

\*Sources with  $\tau_{9.7\mu\text{m}} > 2 \times \tau_{9.0\mu\text{m}}$ , for which an estimated contribution from the CH<sub>3</sub>-rock mode of CH<sub>3</sub>OH was subtracted (see text for details).

### 3. Laboratory work and analysis

The band profiles presented in Fig. 2 contain information on the ice environment in which  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  are located, and thus their formation and processing history. To extract this information, a systematic laboratory study of the  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  features in a variety of ices has been carried out. Specifically, three features between 8 and 10  $\mu\text{m}$  have been analyzed:

1. the  $\text{NH}_3$   $\nu_2$  umbrella mode, at  $\sim 9.35$   $\mu\text{m}$  or  $1070$   $\text{cm}^{-1}$  in pure  $\text{NH}_3$  ice, and with band strength  $A_{\text{pure}} = 1.7 \times 10^{-17}$   $\text{cm molecule}^{-1}$  (d’Hendecourt & Allamandola 1986),
2. the  $\text{CH}_3\text{OH}$   $\nu_4$  CO-stretching mode, at  $\sim 9.74$   $\mu\text{m}$  or  $1027$   $\text{cm}^{-1}$  in pure  $\text{CH}_3\text{OH}$  ice, and with  $A_{\text{pure}} = 1.8 \times 10^{-17}$   $\text{cm molecule}^{-1}$  (d’Hendecourt & Allamandola 1986),
3. the  $\text{CH}_3\text{OH}$   $\nu_7$   $\text{CH}_3$  rocking mode, at  $\sim 8.87$   $\mu\text{m}$  or  $1128$   $\text{cm}^{-1}$  in pure  $\text{CH}_3\text{OH}$  ice, and with  $A_{\text{pure}} = 1.8 \times 10^{-18}$   $\text{cm molecule}^{-1}$  (Hudgins et al. 1993).

It should be noted that, as mentioned in the above list, the quoted positions are for pure ices only and therefore slightly deviate from the astronomical values given in Table 1.

This laboratory study targeted pure, binary and tertiary interstellar ice analogs consisting of different mixtures of  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CO}$  and  $\text{CO}_2$ , the major ice components. All measurements were performed under high vacuum conditions ( $\sim 10^{-7}$  mbar) using an experimental approach described in Gerakines et al. (1995), Bouwman et al. (2007) and Öberg et al. (2007). The ice spectra were recorded in transmission using a Fourier transform infrared spectrometer covering  $25\text{--}2.5$   $\mu\text{m}$  ( $400\text{--}4000$   $\text{cm}^{-1}$ ) with  $1$   $\text{cm}^{-1}$  resolution and by sampling relatively thick ices, typically several thousands Langmuir<sup>1</sup> (L) thick. These ices were grown at a speed of  $\sim 10^{16}$   $\text{molecules cm}^{-2} \text{ s}^{-1}$  on a temperature-controlled CsI window.

<sup>1</sup>One Langmuir corresponds to a pressure of  $10^{-6}$  torr for 1 second and measures the exposure of a surface to adsorption of gases. One Langmuir is equivalent to about  $10^{15}$   $\text{molecules cm}^{-2}$ .

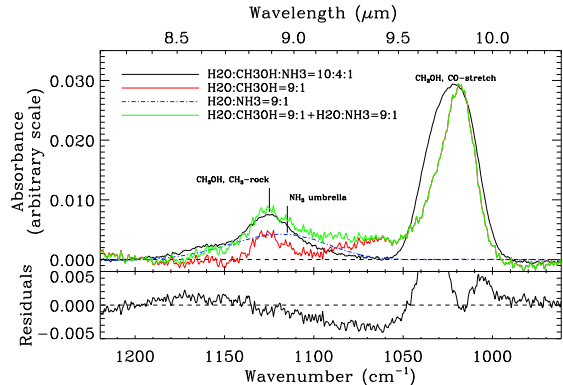


Fig. 5.— Example of a reduced laboratory spectrum (solid black line) for a  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3 = 10:4:1$  ice mixture at 15 K, in the  $8\text{--}10$   $\mu\text{m}$  /  $960\text{--}1220$   $\text{cm}^{-1}$  range. This spectrum can be approximated as the sum (solid green/dark grey line) of  $\text{H}_2\text{O}:\text{CH}_3\text{OH} = 9:1$  (solid red/light grey line) and  $\text{H}_2\text{O}:\text{NH}_3 = 9:1$  (dash-dot blue/grey line). The bottom plot is the difference between the two, showing that the feature at  $9$   $\mu\text{m}$  (blend of  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$   $\text{CH}_3$ -rock modes) is well reproduced by the sum of the two individual signatures. This figure also illustrates the fact that the positions of the features in mixed ices differ from that in pure ices (see list at the beginning of this section).

A typical reduced spectrum for an ice mixture containing  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3 = 10:4:1$  at 15 K is shown in Fig. 5. Since band profiles and strengths change with ice composition and also with temperature, the three fundamentals mentioned above were investigated as a function of temperature ranging from 15 to 140 K with regular temperature steps for a number of binary and tertiary mixtures (listed in Appendix B). An IDL routine was used to determine the location of the band maximum, FWHM and integrated absorbance of the individual absorption bands. For the asymmetric  $\text{NH}_3$   $\nu_2$  umbrella mode the band position has been determined by the maximum absorbance and for the symmetric profiles the spectral parameters have been determined from Gaussian fits of baseline subtracted spectra. The resulting absolute frequency uncertainty is of the order of  $1$   $\text{cm}^{-1}$ . The measurements are presented in Table B.3 of Appendix B, and are included in the Leiden labo-

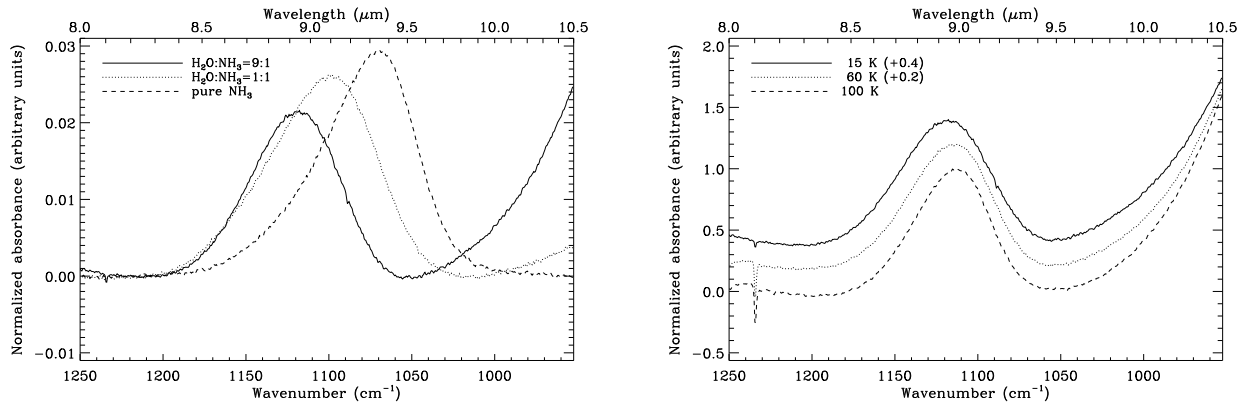


Fig. 6.— (*Left*) FTIR ice spectra of the  $\nu_{\text{NH}_3}$  mode for pure  $\text{NH}_3$ , a  $\text{H}_2\text{O}:\text{NH}_3=1:1$  and a  $\text{H}_2\text{O}:\text{NH}_3=9:1$  mixture at a temperature of 15 K. At the low frequency side of the spectrum the  $\text{H}_2\text{O}$  libration mode (centered around  $770\text{ cm}^{-1}$ , or  $13\text{ }\mu\text{m}$ ) starts showing up for the  $\text{H}_2\text{O}$ -containing mixtures. — (*Right*) Temperature effect on a  $\text{H}_2\text{O}:\text{NH}_3=9:1$  mixture: decreasing FWHM with increasing temperature.

ratory database<sup>2</sup>.

$\text{NH}_3$  and  $\text{CH}_3\text{OH}$  both have the ability to form hydrogen bonds in water-rich matrices, so it is not surprising that the band profile changes compared with pure ices because of the various molecular interactions (e.g., d’Hendecourt & Allamandola 1986)

In addition to profiles, band strengths can change with environment and with temperature, as discussed for the cases of CO and  $\text{CO}_2$  in water-rich ices in Kerkhof et al. (1999); Öberg et al. (2007); Bouwman et al. (2007). Figure 6 shows how the  $\text{NH}_3$   $\nu_2$  umbrella mode absorption maximum shifts from  $1070\text{ cm}^{-1}$  ( $9.35\text{ }\mu\text{m}$ ) for pure  $\text{NH}_3$  ice to  $1118\text{ cm}^{-1}$  ( $8.94\text{ }\mu\text{m}$ ) for an astrophysically more realistic  $\text{H}_2\text{O}:\text{NH}_3=9:1$  (hereafter 9:1) mixture, for which the FWHM and integrated band strength also change significantly. For example, the band strength is lowered in the 9:1 mixture to 70% of its initial value in pure  $\text{NH}_3$  ice. This is in good agreement with previous experiments performed by Kerkhof et al. (1999). The spectral appearance also depends on temperature; for the 9:1 mixture a temperature increase from 15 to 120 K results in a redshift of the peak position from  $1118$  to  $1112\text{ cm}^{-1}$  ( $8.94$  to  $8.99\text{ }\mu\text{m}$ ) and the FWHM decreases from  $62$  to  $52\text{ cm}^{-1}$  ( $0.50$  to  $0.42\text{ }\mu\text{m}$ ) (see Fig. 7). The  $\text{NH}_3$  bandstrength, on the other hand, does not show any temperature

dependence.

If  $\text{NH}_3$  is in a water-poor environment with CO and/or  $\text{CO}_2$ , the  $\nu_2$  peak position shifts to the red compared with pure  $\text{NH}_3$ , to as much as  $1062\text{ cm}^{-1}$  ( $9.41\text{ }\mu\text{m}$ ). The FWHM is not much affected whereas the band strength is lowered by 20%. Because of the intrinsically large difference in band maximum position between  $\text{NH}_3$  in a water-poor and water-rich environment, the astronomical observations can distinguish between these two scenarios.

Methanol-containing ices have been studied in a similar way (see Fig. 8). The weakly absorbing  $\nu_7$   $\text{CH}_3$  rocking mode at  $\sim 1125\text{ cm}^{-1}$  ( $8.89\text{ }\mu\text{m}$ ) is rather insensitive to  $\text{H}_2\text{O}$  mixing, but the  $\nu_4$  CO stretch vibration shifts to the red from  $1028$  to  $1020\text{ cm}^{-1}$  ( $9.73$  to  $9.80\text{ }\mu\text{m}$ ) when changing from a pure  $\text{CH}_3\text{OH}$  ice to a  $\text{H}_2\text{O}:\text{CH}_3\text{OH}=9:1$  mixture. In the latter spectrum the  $\text{CH}_3\text{OH}$   $\nu_4$  CO stretch mode needs to be fitted with a double Gaussians. A substructure appears for a temperature of 80 K (right panel of Fig. 8) while for even higher temperatures, a clearly double peaked structure becomes visible (as previously seen in e.g. Fig. 2 of Schutte et al. 1991). This splitting hints at different physical sites and has been previously ascribed to type II clathrate formation in the ice (Blake et al. 1991).

When  $\text{CH}_3\text{OH}$  is mixed with CO, the band maximum shifts from  $1028$  to  $1034\text{ cm}^{-1}$  ( $9.73$  to  $9.67\text{ }\mu\text{m}$ ) when going from a 9:1 to a 1:9

<sup>2</sup><http://www.strw.leidenuniv.nl/~lab/>

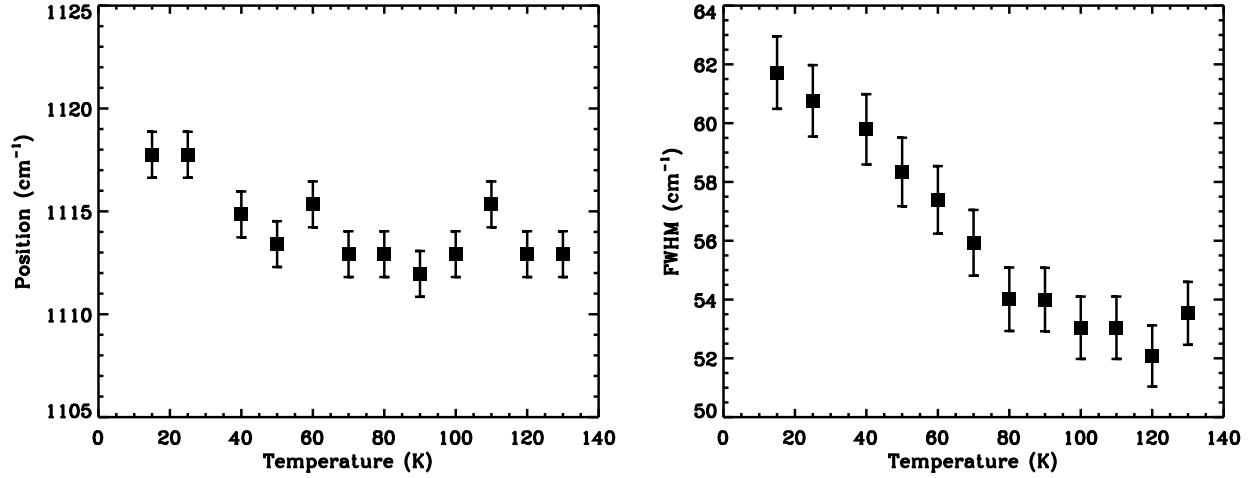


Fig. 7.— A plot indicating the changes in peak position (left) and FWHM (right) of the  $\text{NH}_3$   $\nu_2$  umbrella mode as a function of temperature in a 9:1  $\text{H}_2\text{O}:\text{NH}_3$  ice.

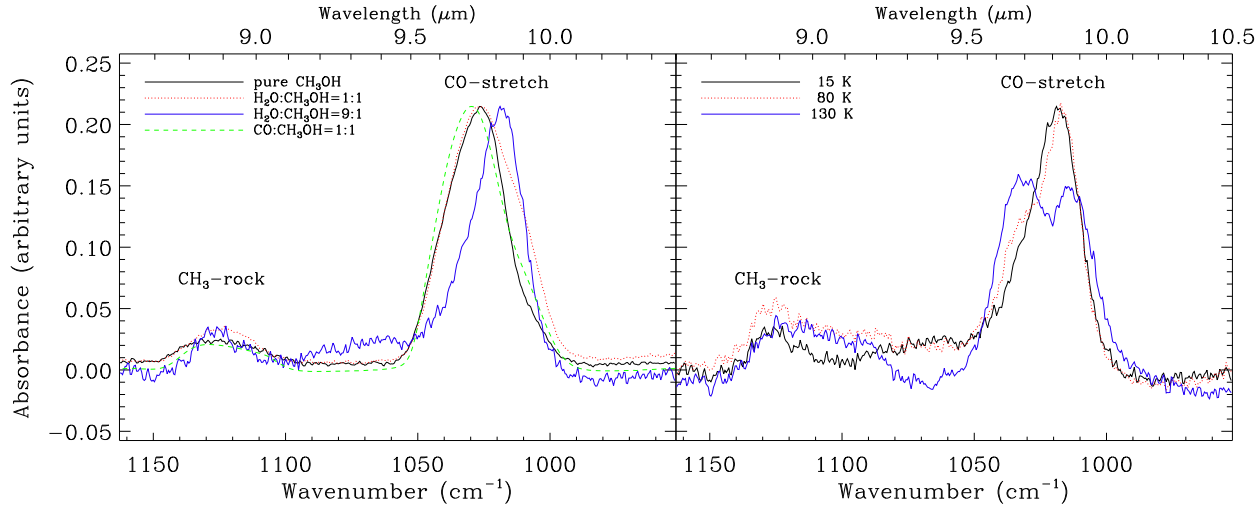


Fig. 8.— (*Left*) Spectra of the  $\text{CH}_3\text{OH}$   $\nu_{\text{CO}}$  modes and  $\nu_{\text{CH}_3}$  modes for pure  $\text{CH}_3\text{OH}$ , a  $\text{H}_2\text{O}:\text{CH}_3\text{OH}=1:1$ , a  $\text{H}_2\text{O}:\text{CH}_3\text{OH}=9:1$  and a  $\text{CO}:\text{CH}_3\text{OH}=1:1$  ice mixture at a temperature of 15 K. — (*Right*) Temperature effect on the CO-stretch mode of a  $\text{H}_2\text{O}:\text{CH}_3\text{OH}=9:1$  mixture.

$\text{CH}_3\text{OH}:\text{CO}$  mixture. When 50% or more CO is mixed in, the  $\text{CH}_3\text{OH}$   $\nu_4$  CO stretch mode starts to show a shoulder and cannot be fitted correctly by a single Gaussian component (see Fig. 9). Such a two-component profile would not be recognized, however, at the spectral resolution and signal/noise of our *Spitzer* data, so for the compari-

son between laboratory and observational data a single Gaussian is used. Overall, the shifts of the  $\text{CH}_3\text{OH}$   $\nu_4$  mode between water-rich and CO-rich mixtures are much smaller than in the case of the  $\text{NH}_3$   $\nu_2$  mode.

The effect of  $\text{CH}_3\text{OH}$  on the  $4.7\mu\text{m}$   $\nu_1$  stretch mode of CO has also been investigated. The band

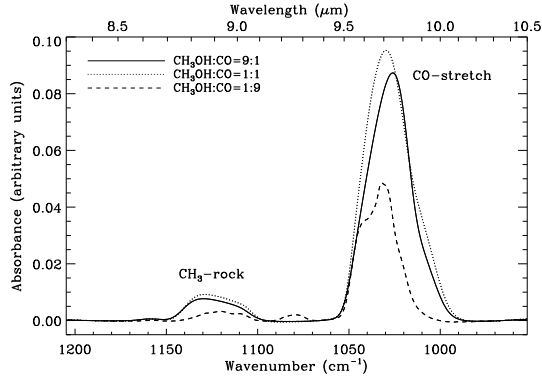


Fig. 9.— Spectra of  $\text{CH}_3\text{OH}:\text{CO}$  mixtures in the range of the methanol CO stretch mode and the methanol  $\text{CH}_3$  rock mode. A small blue shift together with a clear substructure are seen upon mixing in more CO.

maximum shifts from  $2139\text{ cm}^{-1}$  ( $4.68\text{ }\mu\text{m}$ ) for the nearly pure 9:1  $\text{CO}:\text{CH}_3\text{OH}$  mixture to  $2136$  and  $2135\text{ cm}^{-1}$  for the 1:1 and 1:9 mixtures, respectively. The CO band located at  $2136\text{ cm}^{-1}$  is often referred to as CO residing in a polar, mainly  $\text{H}_2\text{O}$  ice, environment. Clearly, the polar  $\text{CH}_3\text{OH}$  molecules can also contribute to CO absorption at  $2136\text{ cm}^{-1}$  when intimately mixed in an astronomical ice.

Binary mixtures of  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  have been studied as well. The  $\text{CH}_3\text{OH}$  modes behave very much as they do in a pure methanol ice, but the  $\text{NH}_3$   $\nu_2$  umbrella mode is clearly suppressed. Its integrated absorbance is readily reduced to 70% of the integrated absorbance of pure  $\text{NH}_3$  in a  $\text{CH}_3\text{OH}:\text{NH}_3=1:1$  mixture and becomes even lower for a 4:1 binary composition. The  $\text{NH}_3$  band also broadens compared to pure  $\text{NH}_3$  or  $\text{H}_2\text{O}:\text{NH}_3$  mixtures and strongly overlaps with the CO stretching mode of  $\text{CH}_3\text{OH}$ , to the level that it becomes difficult to measure.

A qualitative comparison with the astronomical data (see Section 4) indicates that neither pure  $\text{NH}_3$ ,  $\text{CH}_3\text{OH}$ , nor mixed  $\text{CH}_3\text{OH}:\text{NH}_3$  or  $\text{H}_2\text{O}$ -diluted binary ices can simultaneously explain the different  $\text{NH}_3$  profiles in the recorded *Spitzer* spectra. Thus, a series of tertiary mixtures with  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3$  in ratios 10:4:1, 10:1:1 and 10:0.25:1 have been measured, because  $\text{CH}_3\text{OH}$  is the next major ice compo-

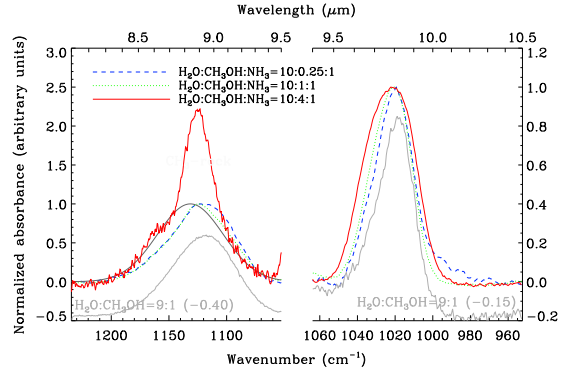


Fig. 10.— Normalized spectra of the  $\text{CH}_3\text{OH}$   $\nu_4$  C–O mode (right panel), and  $\text{NH}_3$   $\nu_2$  umbrella mode (left panel) for a  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3=10:0.25:1$ , a  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3=10:1:1$  and a  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3=10:4:1$  mixture at a temperature of 15 K. These mixture ratios span the range of observed interstellar column density ratios. Spectra were normalized to better show the changes in band maximum position and FWHM of each feature. Spectra of a  $\text{H}_2\text{O}:\text{CH}_3\text{OH}=9:1$  and a  $\text{H}_2\text{O}:\text{NH}_3=1:1$  mixture were offset and overlaid in light grey in the right and left panel, respectively. In the case of  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3=10:4:1$ , the  $\text{NH}_3$   $\nu_2$  umbrella mode is heavily blended with the  $\text{CH}_3\text{OH}$   $\nu_7$   $\text{CH}_3$  rocking mode, so that the dark grey line actually shows the Gaussian fit to the underlying  $\text{NH}_3$  feature, whereas the full  $9\text{-}\mu\text{m}$  feature is shown in black.

nent. These ratios roughly span the range of observed interstellar column density ratios. In Fig. 10, the spectra of  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3$  tertiary mixtures are plotted and compared to binary  $\text{H}_2\text{O}:\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}:\text{NH}_3$  data. The  $\text{NH}_3$   $\nu_2$  umbrella mode shifts slightly to the blue in the presence of both  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$ , with an absorption maximum at  $1125\text{ cm}^{-1}$  ( $8.90\text{ }\mu\text{m}$ ) for the 10:4:1  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3$  mixture (compared to  $1118\text{ cm}^{-1}$  ( $8.94\text{ }\mu\text{m}$ ) in the  $\text{H}_2\text{O}:\text{NH}_3=9:1$  mixture). The peak intensity of the  $\text{NH}_3$   $\nu_2$  umbrella mode band in this tertiary mixture is small compared with that of the  $\text{CH}_3\text{OH}$   $\text{CH}_3$  rock mode, but its integrated intensity is a factor of two larger because of the larger  $\text{NH}_3$  width.

The  $\nu_4$  C–O stretching vibration profile of  $\text{CH}_3\text{OH}$  in the tertiary mixture does not differ

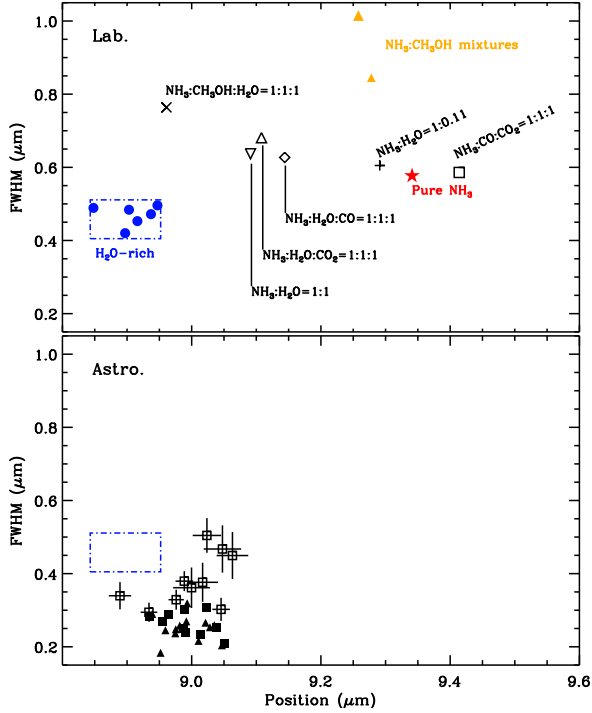


Fig. 11.— FWHM and band maximum position of the  $\text{NH}_3$  feature measured in the laboratory mixtures at 15 K (“Lab.”, top panel) and in the *Spitzer* spectra (“Astro.”, bottom panel). In the top panel, the symbols are labelled with their corresponding mixtures; for the  $\text{NH}_3:\text{CH}_3\text{OH}$  mixtures (orange triangles), an increasing symbol size is indicative of increasing  $\text{CH}_3\text{OH}$  content. In the bottom panel, open and filled squares indicate values obtained with the template and local continuum method, respectively. In both panels, the dash-dot polygons delimitate the parameter space of FWHM and positions corresponding to  $\text{H}_2\text{O}$ -rich mixtures.

much from the binary values for the highest water content. The position of the absorption maximum is also only marginally affected by the temperature. The FWHM decreases from  $30\text{ cm}^{-1}$  ( $0.29\text{ }\mu\text{m}$ ) for the 10:4:1 mixture to  $22\text{ cm}^{-1}$  ( $0.21\text{ }\mu\text{m}$ ) for the 10:0.25:1 mixture.

Besides  $\text{H}_2\text{O}$ , other species may also be regarded as potential candidates for changing the spectral appearance of the  $\text{NH}_3$  and/or  $\text{CH}_3\text{OH}$  features. Chemically linked is  $\text{HCOOH}$  (Bisschop et al. 2007) which unfortunately cannot be deposited in the present setup because of its reactive behavior when mixed with  $\text{NH}_3$ . Tertiary mixtures with  $\text{CO}$  and  $\text{CO}_2$ , two other important constituents in interstellar ices, have been measured (see Appendix B) but here the differences are small compared with the observed binary water-rich or  $\text{CO}$ -

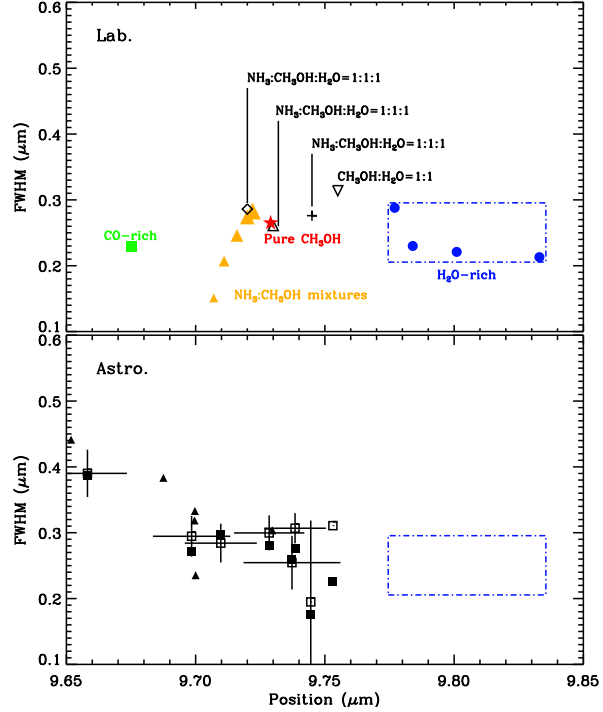


Fig. 12.— Same as Fig. 11 but for  $\text{CH}_3\text{OH}$ .

rich mixtures, and do not offer an alternative explanation.

#### 4. Comparison between astronomical and laboratory data

##### 4.1. 8–10 $\mu\text{m}$ range

The FWHM and band positions of the  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  features measured in the laboratory and astronomical spectra are shown in Figs. 11 (for  $\text{NH}_3$ ) and 12 (for  $\text{CH}_3\text{OH}$ ). For the YSOs, the values obtained after removal of the silicate absorption (see Section 2) using the local continuum method are indicated by filled squares, whereas those obtained from the template method are plotted with open squares. Note that the presence of significant amounts of  $\text{CH}_3\text{OH}$  may artificially

lower the inferred  $\text{NH}_3$   $\nu_2$  width in  $\text{CH}_3\text{OH}$  rich sources (indicated with \* in Table 2) because of the contribution of the narrower  $\nu_7$   $\text{CH}_3$ -rock mode.

Regardless of the method used to subtract the continuum, or the type of source ( $\text{CH}_3\text{OH}$ -rich/poor), we find that the observational band positions and FWHM of the  $\nu_2$   $\text{NH}_3$  umbrella mode absorptions vary, within the errors, between 8.9 and 9.1  $\mu\text{m}$  and between  $\sim 0.2$  and 0.5  $\mu\text{m}$ , respectively. These position and width are not well simultaneously reproduced by any of the investigated mixtures. Regarding the positions, those measured in water-rich ice mixtures are the closest, whereas the positions in pure  $\text{NH}_3$  or  $\text{CO}/\text{CO}_2$  rich ices are too far away to be representative of the astronomical positions. The derived *Spitzer* FWHM values range between 0.23 and 0.32  $\mu\text{m}$  (except for B1-b : 0.39  $\mu\text{m}$ ), when using the local continuum method, not depending on whether the target is  $\text{CH}_3\text{OH}$ -rich or -poor. For the template method,  $\text{CH}_3\text{OH}$ -rich sources generally tend to have a narrower inferred FWHM, 0.3–0.5  $\mu\text{m}$ , contrary to what would be expected if the  $\text{NH}_3$  mode is contaminated by the  $\text{CH}_3$ -rock feature. In any case, most of these widths are still narrower than the laboratory FWHM values. To investigate further the effect of the continuum on the positions and widths of the bands, we performed the following alternative analysis to check whether a continuum could be found that would yield  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  features with parameters within the laboratory measurements. To do that, we fitted the data between 8.25 and 10.4  $\mu\text{m}$  with a function that is the sum of a 4<sup>th</sup> order polynomial and two gaussians ; positions and widths of the gaussians were constrained with limits taken from the laboratory data of binary water mixtures (8.9–8.95  $\mu\text{m}$  for the  $\text{NH}_3$  position, 0.42–0.52  $\mu\text{m}$  for its width; 9.67–9.77  $\mu\text{m}$  for the  $\text{CH}_3\text{OH}$  position, 0.2–0.3  $\mu\text{m}$  for its width). As illustrated in Fig. 13, we found that the continuum derived in this way is different from those determined via the other two methods. This result supports the fact that the difference between astronomical and laboratory data could be attributed to the uncertainty in the continuum determination.

Taking the above considerations into account, Figs. 11 and 12 suggest that the template method for subtraction of the 10  $\mu\text{m}$  silicate absorption is more consistent with the laboratory measure-

ments, but both methods probably miss some weak  $\text{NH}_3$  absorption features in the broad line wings where they blend with the continuum at the  $S/N$  of the data. If so, the too small line widths inferred from the data (most probably due to the uncertainty in the continuum determination) would mean that we have underestimated  $\text{NH}_3$  abundances by a up to a factor of 2.

The observational band position and FWHM of the  $\text{CH}_3\text{OH}$  features derived with either the local continuum or template method are clustered around 9.7–9.75  $\mu\text{m}$ , with the exception of R CrA IRS 5 at 9.66  $\mu\text{m}$ . Similarly the FWHM of the  $\text{CH}_3\text{OH}$  features are all very similar between  $\sim 0.22$  and 0.32  $\mu\text{m}$ , except for R CrA IRS 5 with 0.39  $\mu\text{m}$ . These values agree (with a few exceptions) with the values obtained from the laboratory spectra. Note that the observed positions of the  $\text{CH}_3\text{OH}$  feature are all on the low side of the laboratory range. Since the position of this feature shifts to higher wavelengths with increasing water content, the observed low values could therefore indicate that  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$  are not well mixed and that there exists a separate  $\text{CH}_3\text{OH}$ -rich component, as suggested in previous work (e.g. Pontoppidan et al. 2003; Skinner et al. 1992). Alternatively, the low values could be due to the presence of  $\text{CO}$  as indicated by the  $\text{CH}_3\text{OH}$  feature shift to 9.70  $\mu\text{m}$  in  $\text{CH}_3\text{OH}:\text{CO}=1:1$ . Both interpretations would be consistent with the bulk of the  $\text{CH}_3\text{OH}$  formation coming from hydrogenation of a  $\text{CO}$ -rich layer, rather than photochemistry in a water-rich matrix. However, the shift from the water-rich mixtures is small, and some water-rich fraction cannot be excluded with the current spectral resolution.

#### 4.2. The 3 and 6 $\mu\text{m}$ ranges

Dartois & d’Hendecourt (2001) discussed the possibility of a 3.47  $\mu\text{m}$  absorption band which could be related to the formation of an ammonia hydrate in the ice mantles: they found that if this band were mostly due to this hydrate, then ammonia abundances would be at most 5% with respect to water ice. Considering the fact that our derived abundances are larger than 10% in some sources, it is necessary to investigate the effect of such a high abundance on the ammonia features in other spectral ranges. For this, depending on the  $\text{NH}_3$ -to- $\text{CH}_3\text{OH}$  abun-



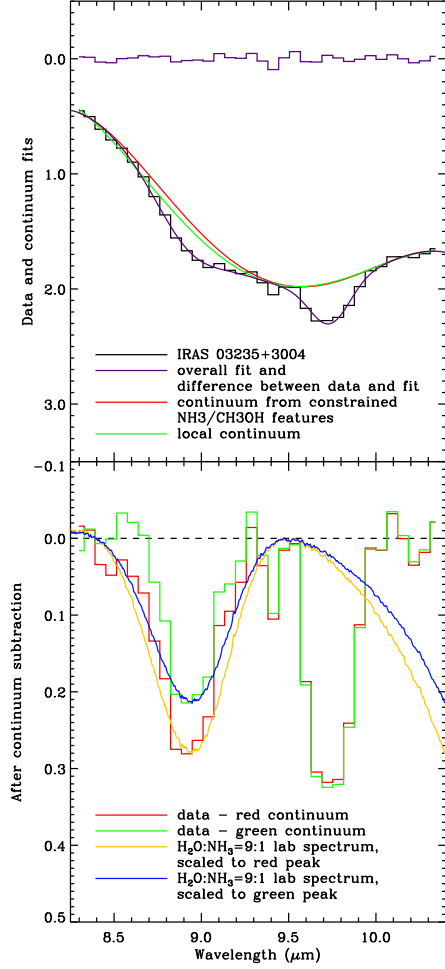


Fig. 13.— Example of the effect of continuum determination. *Upper panel:* Spectrum of IRAS 03235+3004 in the 8.25–10.4  $\mu\text{m}$  region overlaid with the overall fit (smooth purple line – sum of a 4<sup>th</sup> order polynomial and two gaussians with positions and widths constrained by the values measured in the laboratory spectra of  $\text{H}_2\text{O}:\text{NH}_3$  and  $\text{CH}_3\text{OH}$  mixtures), the 4<sup>th</sup> order polynomial obtained by the overall fit (red) and the local continuum previously determined (green). The purple histogram is the difference between the data and the overall fit. — *Bottom panel:* Residuals after subtraction of the two continua, in respective colors. The yellow and blue lines are  $\text{H}_2\text{O}:\text{NH}_3=9:1$  laboratory spectra scaled to the red and green residuals, respectively. Note the good agreement between the feature extracted with the red continuum and the lab data (orange) showing that astronomical and laboratory data of  $\text{NH}_3$  ice mixtures can be consistent if a slightly different continuum determination is adopted.

dance ratio observed in the *Spitzer* spectra, we scale one of the following laboratory spectra to the 9  $\mu\text{m}$   $\text{NH}_3$  feature:  $\text{H}_2\text{O}:\text{NH}_3=9:1$ ,  $\text{H}_2\text{O}:\text{NH}_3=4:1$ ,  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3=10:1:1$ ,  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3=10:4:1$ . Figure 14 illustrates the comparison between the *Spitzer* and scaled laboratory spectra for the relevant wavelength ranges for a couple of sources, while Fig. C.1-a and -b (see Appendix B) show the comparison for all sources where  $\text{NH}_3$  was tentatively detected.

For further comparison, we also overplotted in Fig. 14 and C.1, the following spectra: (i) the pure  $\text{H}_2\text{O}$  ice spectrum derived from the  $\text{H}_2\text{O}$  column density quoted in Boogert et al. (2008) (deep blue); and (ii) for sources with 3  $\mu\text{m}$  data, the pure  $\text{H}_2\text{O}$  spectrum scaled to the optical depth of the 3- $\mu\text{m}$  feature of the mixed ice laboratory

spectrum (purple-dotted). The difference between this scaled pure water spectrum and the mixed ice spectrum gives an indication of the contribution of ammonia features around 3.47 and 6.1  $\mu\text{m}$ .

We then determined the contributions from the  $\text{NH}_3$  features to the integrated optical depths of the 3 and 6  $\mu\text{m}$  bands and to the optical depth of component C2, a feature at 6.0 – 6.4  $\mu\text{m}$  arising from a blend of several species, including  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{HCOO}^-$  (see Paper I for more details). These contributions are reported in Table 3.

Figure 14, C.1 and Table 3 show that (i) the scaled laboratory spectra *generally* do not overestimate the observed absorption features, and (ii) for most sources, the presence of  $\text{NH}_3$  at the level we determine from the 9  $\mu\text{m}$  feature does not explain by itself the depth of the C2 component and

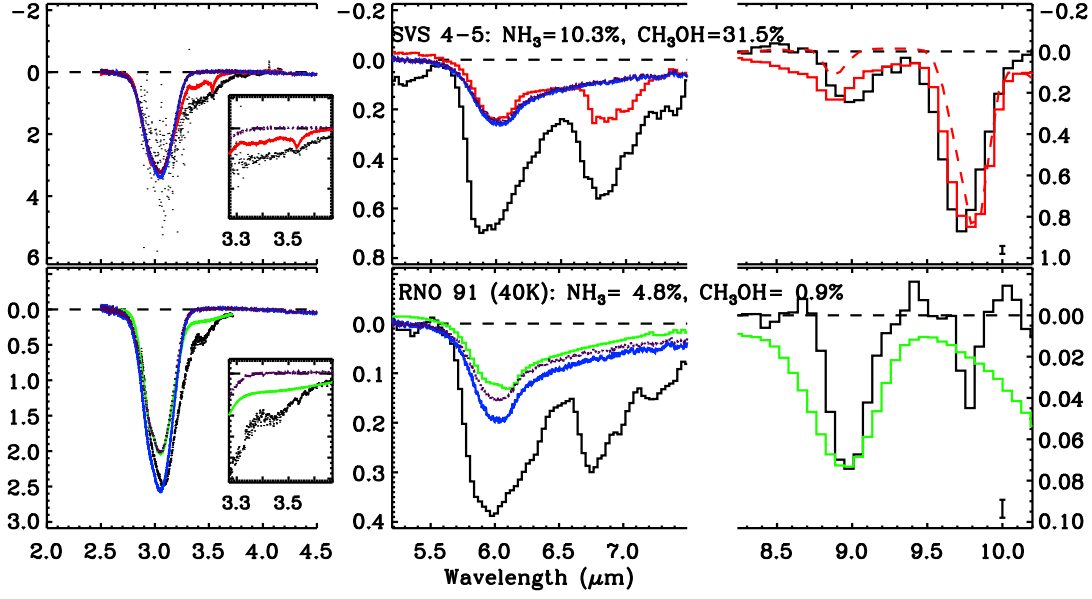


Fig. 14.— Comparison of astronomical data (VLT or Keck measurements at short wavelengths, IRS *Spitzer* observations elsewhere) and laboratory spectra in selected wavelength ranges: 2.0 – 4.5  $\mu\text{m}$  (left panels), 5.2 – 7.5  $\mu\text{m}$  (middle panels) and 8.2 – 10.2  $\mu\text{m}$  (right panels, silicate absorption subtracted via the template method). Error bars are indicated in the bottom-right corner. Overlaid in red and green are laboratory spectra corresponding to  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3=10:4:1$  and  $\text{H}_2\text{O}:\text{NH}_3=9:1$ , respectively, scaled to the 9- $\mu\text{m}$   $\text{NH}_3$  umbrella mode, and smoothed to the *Spitzer* resolution in the  $\sim 5 - 10 \mu\text{m}$  range. The dark blue line represents the pure water laboratory spectrum scaled to the water column density taken in paper I. The dotted purple line corresponds to a pure water spectrum scaled to the 3- $\mu\text{m}$  water feature of the mixed ice spectrum, showing the contribution of  $\text{NH}_3$  features around 3.47 and 6.1  $\mu\text{m}$ . Finally, the red dashed line in the right panel of SVS 4-5 represents a  $\text{H}_2\text{O}:\text{CH}_3\text{OH}=9:1$  laboratory spectrum scaled to the 9.7- $\mu\text{m}$   $\text{CH}_3\text{OH}$  CO-stretch mode: this gives an indication of the contribution of the 9- $\mu\text{m}$   $\text{CH}_3\text{OH}$   $\text{CH}_3$ -rock mode to the total 9- $\mu\text{m}$  feature. The laboratory spectra are recorded at 15 K unless indicated differently.

TABLE 3  
NH<sub>3</sub> CONTRIBUTION TO THE 3 AND 6  $\mu$ M BANDS

Source	$\frac{\int \tau_{\text{H}_2\text{O},3.0}}{\int \tau_{3.0}}$	$\frac{\int \tau_{\text{mix},3.0}}{\int \tau_{3.0}}$	$\frac{\int_{1562}^{1785} \tau_{\text{H}_2\text{O}}}{\int_{1562}^{1785} \tau}$	$\frac{\int_{1562}^{1785} \tau_{\text{mix}}}{\int_{1562}^{1785} \tau}$	$\frac{\int \tau_{\text{NH}_3,6.16}}{\int_{1562}^{1785} \tau_{\text{H}_2\text{O}}}$	$\frac{\tau_{\text{NH}_3,6.16}}{\tau_{\text{C2}}}$
Sources with template						
IRAS 03235+3004	—	—	0.50	0.24	0.02	0.61
IRAS 03254+3050	0.73	1.30	0.56	0.92	0.12	1.72
IRAS 04108+2803	0.70	0.67	0.58	0.53	0.06	0.49
HH 300	0.70	0.57	0.50	0.39	0.05	0.45
IRAS 08242-5050	0.76	0.72	0.50	0.45	0.06	0.46
IRAS 08242-5050	0.76	0.56	0.50	0.35	0.05	0.36
2MASSJ17112317-272431	—	—	0.69	0.53	0.05	4.23
SVS 4-5	0.91	0.94	0.42	0.29	0.00	0.08
R CrA IRS 5	0.85	0.42	0.63	0.29	0.03	0.21
Sources with no associated template						
RNO 15	0.80	1.97	0.53	1.23	0.16	0.45
IRAS 03271+3013	—	—	0.36	0.44	0.05	0.60
B1-a	—	—	0.67	0.43	0.03	0.57
L1489 IRS	0.78	0.88	0.60	0.56	0.04	0.83
RNO 91	0.94	0.94	0.53	0.45	0.04	0.53
IRAS 17081-2721	0.65	0.95	0.62	0.75	0.05	1.64
EC 74	0.95	2.34	0.57	1.18	0.09	0.76
EC 92	0.90	0.35	0.38	0.10	0.00	0.01
CrA IRS7 B	—	—	0.81	0.19	0.00	0.08
L1014 IRS	—	—	0.62	0.55	0.06	0.34

NOTE.—A dash indicates that the ratio was not calculated due to the high noise in the 3- $\mu$ m spectrum.  
Parameters are:  
 $\int \tau_{\text{H}_2\text{O},3.0}$  = integrated optical depth of pure water at 3  $\mu$ m, determined from the column density of paper I and a band strength of  $2.0 \times 10^{-16} \text{ cm}^{-1}$ .  
 $\int \tau_{3.0}$ ,  $\int \tau_{\text{mix},3.0}$  = integrated optical depth over the entire 3  $\mu$ m region for, respectively, the considered source and the corresponding laboratory mixture (selected from the NH<sub>3</sub> feature at 9  $\mu$ m).  
 $\int_{1562}^{1785} \tau_{\text{H}_2\text{O}}$ ,  $\int_{1562}^{1785} \tau$ ,  $\int_{1562}^{1785} \tau_{\text{mix}}$  = integrated optical depth of, respectively, pure water, source spectrum, and laboratory mixture, between 1562 and 1785  $\text{cm}^{-1}$  (5.6 to 6.4  $\mu$ m).  
 $\int \tau_{\text{NH}_3,6.16}$ ,  $\tau_{\text{NH}_3,6.16}$  = integrated and peak optical depth of the 6.16  $\mu$ m feature of ammonia obtained after subtraction of a pure water spectrum scaled to the optical depth at 3  $\mu$ m of the laboratory mixture.  
 $\tau_{\text{C2}}$  = peak optical depth of the C2 component from paper I.

of the red wing of the 3  $\mu\text{m}$  band. Hence, our inferred  $\text{NH}_3$  abundances up to 15% from the 9.7  $\mu\text{m}$  data are not in conflict with the lack of other  $\text{NH}_3$  features. The only exceptions are two sources (RNO 15 and EC 74), for which the scaled mixed ice spectrum exceeds the data in the 3- $\mu\text{m}$  range. In the case of RNO 15, the  $\text{NH}_3$  abundance could have been overestimated due to the contribution of the  $\text{CH}_3\text{OH}$   $\text{CH}_3$ -rock feature at  $\sim 9 \mu\text{m}$ . For EC 74, this overestimate and the presence of emission weakens the identification of the  $\text{NH}_3$  signature. In both cases, the quoted  $\text{NH}_3$  abundances should be considered as upper limits.

Overall, our reported  $\text{NH}_3$  abundances are up to a factor of three larger than the upper limits derived by Dartois & d'Hendecourt (2001). Firstly, let's recall that the conclusions in their study and in ours are drawn from the analysis of different samples. Secondly, Dartois & d'Hendecourt made an assumption that does not apply to our sample: indeed, they considered a grain size distribution including also scattering from larger grains, producing an enhanced 3- $\mu\text{m}$  wing, whereas the results presented here can be taken as representative of  $\text{NH}_3$  absorption from small grains. It is beyond the scope of this paper to investigate the effects of grain size distribution and scattering in as much detail as did Dartois & d'Hendecourt (2001).

### 4.3. Nitrogen ice inventory

The confirmation of the presence of relatively large amounts of solid  $\text{NH}_3$ , up to 15%, in interstellar ices solves a long-standing problem. Indeed, the detection of solid  $\text{NH}_3$  has remained elusive and/or controversial, despite a number of clues suggesting its presence:

- High cosmic abundance of atomic nitrogen :  $N_{\text{N}}/N_{\text{H}} = 7.76 \times 10^{-5}$  (Savage & Sembach 1996), only a factor of a few below those of oxygen and carbon. Here  $N_{\text{H}}$  indicates the total number of hydrogen nuclei,  $N_{\text{H}} = N(\text{H}) + 2N(\text{H}_2)$ .
- High abundances of gaseous  $\text{NH}_3$  of  $N_{\text{NH}_3}/N_{\text{H}_2} \sim 10^{-6} - 10^{-5}$  in the Orion-KL nebula (Barrett et al. 1977; Genzel et al. 1982) and in other hot cores such as G9.62+0.19, G29.96-0.02, G31.41+0.31 (Cesaroni et al. 1994), and G10.47+0.03 (Cesaroni et al. 1994; Osorio et al. 2009).

- Identification of substantial amounts of  $\text{OCN}^-$  (e.g. van Broekhuizen et al. 2004, 2005) and  $\text{NH}_4^+$  in ices (e.g. Schutte & Khanna 2003; Boogert et al. 2008): considering that these ions form via reactions involving  $\text{NH}_3$ , the non-detection of solid  $\text{NH}_3$  would be puzzling.

Our results can be used to draw up a possible nitrogen budget. Assuming  $N_{\text{H}_2\text{O}}/N_{\text{H}} \sim 5 \times 10^{-5}$  (Pontoppidan et al. 2004; Boogert et al. 2004), and average abundances w.r.t.  $\text{H}_2\text{O}$  of 5.5% for  $\text{NH}_3$  (see §2.3), 7% for  $\text{NH}_4^+$  (from Table 3 of Paper I), and 0.6% for  $\text{OCN}^-$  (van Broekhuizen et al. 2005), then the  $\text{NH}_3$ ,  $\text{NH}_4^+$  and  $\text{OCN}^-$  abundances with respect to total H are 2.8, 3.5, and  $0.3 \times 10^{-6}$  respectively. This corresponds to, respectively, 3.4, 4.4 and 0.4% of the atomic nitrogen cosmic abundance so that, in total, about 10% of the cosmically available nitrogen would be locked up in ices, leaving solid and gaseous  $\text{N}_2$ , N and HCN as other substantial nitrogen carriers. The main uncertainty in this determination is the adopted  $\text{H}_2\text{O}$  ice abundance with respect to total H; in several sources this may well be a factor of 2 larger, leading to about 20% of the nitrogen accounted for in ices.

## 5. Conclusion

We have analyzed in detail the 8-10  $\mu\text{m}$  range of the spectra of 41 low-mass YSOs obtained with *Spitzer* and presented in Boogert et al. (2008). The sources are categorized into three types: straight, curved and rising 8  $\mu\text{m}$  silicate wings, and for each category template sources with little or no absorption from ices around 9-10  $\mu\text{m}$  have been determined. This has led to two ways of subtracting the contribution from the 10  $\mu\text{m}$  silicate absorption: first, by determining a local continuum, and second, by scaling the templates to the optical depth at 9.7  $\mu\text{m}$ . The two methods give consistent band positions of the  $\text{NH}_3$  features, but the resulting widths can be up to a factor of two larger using the template continuum method. Taking into account the uncertainty in continuum determination,  $\text{NH}_3$  ice is most likely detected in 24 of the 41 sources with abundances of  $\sim 2$  to 15 % w.r.t.  $\text{H}_2\text{O}$ , with an average abundance of  $5.5 \pm 2.0$  %. These abundances have estimated uncertainties up to a factor of two and are not

inconsistent with other features in the 3 and 6  $\mu\text{m}$  ranges.  $\text{CH}_3\text{OH}$  is often detected as well, but the  $\text{NH}_3/\text{CH}_3\text{OH}$  abundance ratio changes strongly from source to source. Our inferred  $\text{CH}_3\text{OH}$  column densities are consistent with the values derived in paper I.

Targeted laboratory experiments have been carried out to characterize the  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  profiles (position, FWHM, integrated absorbance). Comparison with the observational data shows reasonable agreement (within  $\sim 1\%$ ) for the position of the  $\text{NH}_3$  feature in  $\text{H}_2\text{O}$ -rich ices, but the observed widths are systematically smaller than the laboratory ones for nearly all sources. The silicate template continuum method gives widths that come closest to the laboratory values. This difference in width (i.e. widths derived from astronomical spectra smaller than those in the laboratory spectra) suggests that the  $\text{NH}_3$  abundances determined here may be on the low side.

The  $\text{CH}_3\text{OH}$  profile is most consistent with a significant fraction of the  $\text{CH}_3\text{OH}$  in a relatively pure or CO-rich phase, consistent with its formation by the hydrogenation of CO ice. In contrast, the most likely formation route of  $\text{NH}_3$  ice remains hydrogenation of atomic N together with water ice formation in a relatively low density molecular phase. Finally, the nitrogen budget indicates that up to 10 to 20 % of nitrogen is locked up in known ices.

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## A. Parameters of Gaussian fits

TABLE A.1  
PARAMETERS OF GAUSSIAN FITS TO THE NH<sub>3</sub> FEATURE.

Source	NH <sub>3</sub> , local			NH <sub>3</sub> , template		
	$\lambda$ ( $\mu\text{m}$ )	FWHM ( $\mu\text{m}$ )	$\tau_{\text{peak}}$	$\lambda$ ( $\mu\text{m}$ )	FWHM ( $\mu\text{m}$ )	$\tau_{\text{peak}}$
IRAS 03235+3004	8.93 $\pm$ 0.02	0.28 $\pm$ 0.03	0.23 $\pm$ 0.02	8.93 $\pm$ 0.01	0.29 $\pm$ 0.03	0.30 $\pm$ 0.02
L1455 IRS3	8.99 $\pm$ 0.03	0.24 $\pm$ 0.07	0.02 $\pm$ 0.01	9.02 $\pm$ 0.02	0.38 $\pm$ 0.05	0.04 $\pm$ 0.01
IRAS 03254+3050	9.04 $\pm$ 0.01	0.25 $\pm$ 0.03	0.10 $\pm$ 0.01	8.99 $\pm$ 0.01	0.38 $\pm$ 0.03	0.12 $\pm$ 0.01
B1-b*	9.05 $\pm$ 0.03	0.39 $\pm$ 0.06	0.25 $\pm$ 0.02	9.07 $\pm$ 0.03	0.40 $\pm$ 0.06	0.31 $\pm$ 0.03
IRAS 04108+2803	8.99 $\pm$ 0.02	0.25 $\pm$ 0.04	0.05 $\pm$ 0.01	9.05 $\pm$ 0.03	0.47 $\pm$ 0.06	0.04 $\pm$ 0.01
HH 300	9.01 $\pm$ 0.02	0.23 $\pm$ 0.05	0.04 $\pm$ 0.01	9.06 $\pm$ 0.02	0.45 $\pm$ 0.06	0.05 $\pm$ 0.01
IRAS 08242-5050	9.02 $\pm$ 0.01	0.31 $\pm$ 0.03	0.15 $\pm$ 0.01	9.05 $\pm$ 0.01	0.30 $\pm$ 0.03	0.15 $\pm$ 0.01
IRAS 15398-3359	8.96 $\pm$ 0.01	0.29 $\pm$ 0.03	0.30 $\pm$ 0.02	8.98 $\pm$ 0.01	0.33 $\pm$ 0.03	0.41 $\pm$ 0.02
B59 YSO5	8.95 $\pm$ 0.01	0.27 $\pm$ 0.03	0.18 $\pm$ 0.02	8.89 $\pm$ 0.02	0.34 $\pm$ 0.04	0.18 $\pm$ 0.02
2MASSJ17112317-272431	8.99 $\pm$ 0.01	0.30 $\pm$ 0.02	0.43 $\pm$ 0.02	9.02 $\pm$ 0.02	0.50 $\pm$ 0.05	0.41 $\pm$ 0.04
SVS 4-5*	9.00 $\pm$ 0.01	0.26 $\pm$ 0.03	0.16 $\pm$ 0.02	9.01 $\pm$ 0.01	0.30 $\pm$ 0.03	0.26 $\pm$ 0.02
R. CrA IRS 5	9.05 $\pm$ 0.02	0.21 $\pm$ 0.04	0.04 $\pm$ 0.01	9.00 $\pm$ 0.03	0.36 $\pm$ 0.06	0.04 $\pm$ 0.01
RNO 15	9.05 $\pm$ 0.02	0.20 $\pm$ 0.04	0.04 $\pm$ 0.01	—	—	—
IRAS 03271+3013	8.96 $\pm$ 0.02	0.25 $\pm$ 0.04	0.20 $\pm$ 0.02	—	—	—
B1-a	8.98 $\pm$ 0.02	0.25 $\pm$ 0.04	0.14 $\pm$ 0.02	—	—	—
L1489 IRS	9.02 $\pm$ 0.01	0.27 $\pm$ 0.03	0.09 $\pm$ 0.01	—	—	—
IRAS 13546-3941	8.99 $\pm$ 0.02	0.27 $\pm$ 0.03	0.03 $\pm$ 0.00	—	—	—
RNO 91	8.98 $\pm$ 0.01	0.26 $\pm$ 0.03	0.08 $\pm$ 0.01	—	—	—
IRAS 17081-2721	8.97 $\pm$ 0.02	0.24 $\pm$ 0.04	0.04 $\pm$ 0.00	—	—	—
EC 74	9.01 $\pm$ 0.02	0.22 $\pm$ 0.05	0.05 $\pm$ 0.01	—	—	—
EC 82	8.94 $\pm$ 0.01	0.29 $\pm$ 0.03	0.04 $\pm$ 0.00	—	—	—
EC 90	8.95 $\pm$ 0.02	0.18 $\pm$ 0.05	0.04 $\pm$ 0.01	—	—	—
EC 92*	8.99 $\pm$ 0.02	0.25 $\pm$ 0.05	0.03 $\pm$ 0.00	—	—	—
CK4	8.99 $\pm$ 0.02	0.32 $\pm$ 0.04	0.03 $\pm$ 0.00	—	—	—
CrA IRS7 B*	9.04 $\pm$ 0.01	0.26 $\pm$ 0.03	0.15 $\pm$ 0.01	—	—	—
L1014 IRS	9.03 $\pm$ 0.02	0.25 $\pm$ 0.05	0.15 $\pm$ 0.02	—	—	—

NOTE.—Uncertainties are statistical errors from the Gaussian fits.

\*Sources with  $\tau_{9.7\mu\text{m}} > 2 \times \tau_{9.0\mu\text{m}}$ , for which the contribution from the CH<sub>3</sub>OH CH<sub>3</sub>-rock mode is significant. Since the latter and the NH<sub>3</sub> umbrella mode were difficult to disentangle, a single fit was performed (the reported parameters) and the integrated optical depth of the ammonia feature was then obtained from the total integrated optical depth at 9  $\mu\text{m}$  by subtracting the estimated contribution of the CH<sub>3</sub>OH CH<sub>3</sub>-rock mode (see §2.2).

TABLE A.2

PARAMETERS OF GAUSSIAN FITS TO THE CH<sub>3</sub>OH C-O STRETCH MODE (AFTER SUBTRACTION OF THE CONTINUUM WITH THE LOCAL AND/OR TEMPLATE METHOD), AND CH<sub>3</sub>OH COLUMN DENSITIES (OR 3- $\sigma$  UPPER LIMITS).

Source	Local continuum				Template continuum				Paper I X (% H <sub>2</sub> O)
	$\lambda$ ( $\mu$ m)	FWHM ( $\mu$ m)	$\tau_{\text{peak}}$	X (% H <sub>2</sub> O)	$\lambda$ ( $\mu$ m)	FWHM ( $\mu$ m)	$\tau_{\text{peak}}$	X (% H <sub>2</sub> O)	
IRAS 03235+3004	9.74 $\pm$ 0.02	0.26 $\pm$ 0.03	0.35 $\pm$ 0.04	4.40 $\pm$ 1.04	9.74 $\pm$ 0.02	0.25 $\pm$ 0.04	0.31 $\pm$ 0.04	3.84 $\pm$ 0.99	4.20 $\pm$ 1.20
L1455 IRS3	9.78 $\pm$ 0.01	0.14 $\pm$ 0.03	0.03 $\pm$ 0.01	3.67 $\pm$ 1.80	9.78 $\pm$ 0.02	0.26 $\pm$ 0.04	0.04 $\pm$ 0.01	7.71 $\pm$ 3.46	<12.5
IRAS 03254+3050	...	...	...	< 5.4	...	...	...	< 5.4	< 4.6
B1-b	9.71 $\pm$ 0.01	0.30 $\pm$ 0.03	1.19 $\pm$ 0.11	14.15 $\pm$ 3.16	9.71 $\pm$ 0.01	0.28 $\pm$ 0.03	1.21 $\pm$ 0.11	13.75 $\pm$ 3.12	11.20 $\pm$ 0.70
IRAS 04108+2803	...	...	...	< 2.7	9.75 $\pm$ 0.00	0.06 $\pm$ 0.04	0.04 $\pm$ 0.03	0.58 $\pm$ 0.62	< 3.5
HH 300	...	...	...	< 4.7	9.74 $\pm$ 0.00	0.19 $\pm$ 0.12	0.01 $\pm$ 0.01	0.78 $\pm$ 0.52	< 6.7
IRAS 08242-5050	9.70 $\pm$ 0.01	0.27 $\pm$ 0.03	0.25 $\pm$ 0.02	6.12 $\pm$ 1.01	9.70 $\pm$ 0.01	0.29 $\pm$ 0.03	0.24 $\pm$ 0.02	6.39 $\pm$ 1.09	5.50 $\pm$ 0.30
IRAS 15398-3359	9.73 $\pm$ 0.01	0.28 $\pm$ 0.03	0.77 $\pm$ 0.06	10.26 $\pm$ 3.02	9.73 $\pm$ 0.01	0.30 $\pm$ 0.03	0.75 $\pm$ 0.06	10.69 $\pm$ 3.14	10.30 $\pm$ 0.80
B59 YSO5	...	...	...	< 1.2	...	...	...	< 1.2	< 1.3
2MASSJ17112317-272431	9.75 $\pm$ 0.02	0.23 $\pm$ 0.04	0.13 $\pm$ 0.02	1.03 $\pm$ 0.22	...	...	...	< 2.0	< 3.2
SVS 4-5	9.74 $\pm$ 0.01	0.28 $\pm$ 0.03	0.77 $\pm$ 0.06	26.38 $\pm$ 6.17	9.74 $\pm$ 0.01	0.31 $\pm$ 0.02	0.83 $\pm$ 0.06	31.50 $\pm$ 7.12	25.20 $\pm$ 3.50
R CrA IRS 5	9.66 $\pm$ 0.01	0.39 $\pm$ 0.03	0.07 $\pm$ 0.00	5.68 $\pm$ 0.60	9.66 $\pm$ 0.02	0.39 $\pm$ 0.04	0.07 $\pm$ 0.00	5.51 $\pm$ 0.72	6.60 $\pm$ 1.60
RNO 15	9.65 $\pm$ 0.03	0.44 $\pm$ 0.07	0.02 $\pm$ 0.00	11.13 $\pm$ 2.16	...	...	...	...	< 5.0
IRAS 03271+3013	...	...	...	< 4.3	...	...	...	...	< 5.6
B1-a	...	...	...	< 2.4	...	...	...	...	< 1.9
L1489 IRS	9.78 $\pm$ 0.02	0.10 $\pm$ 0.03	0.03 $\pm$ 0.01	0.44 $\pm$ 0.22	...	...	...	...	4.90 $\pm$ 1.50
IRAS 13546-3941	...	...	...	< 2.0	...	...	...	...	< 3.9
RNO 91	9.77 $\pm$ 0.01	0.11 $\pm$ 0.03	0.05 $\pm$ 0.01	0.87 $\pm$ 0.32	...	...	...	...	< 5.6
IRAS 17081-2721	...	...	...	< 6.6	...	...	...	...	3.30 $\pm$ 0.80
EC 74	...	...	...	<13.5	...	...	...	...	< 9.3
EC 82	...	...	...	<24.6	...	...	...	...	<14.2
EC 90	9.70 $\pm$ 0.01	0.32 $\pm$ 0.03	0.05 $\pm$ 0.00	6.91 $\pm$ 0.99	...	...	...	...	6.80 $\pm$ 1.60
EC 92	9.73 $\pm$ 0.01	0.30 $\pm$ 0.02	0.09 $\pm$ 0.01	11.16 $\pm$ 1.46	...	...	...	...	11.70 $\pm$ 3.50
CK4	...	...	...	...	...	...	...	...	...
CrA IRS7 B	9.70 $\pm$ 0.01	0.33 $\pm$ 0.02	0.36 $\pm$ 0.02	7.74 $\pm$ 1.56	...	...	...	...	6.80 $\pm$ 0.30
L1014 IRS	9.69 $\pm$ 0.03	0.38 $\pm$ 0.08	0.10 $\pm$ 0.01	3.61 $\pm$ 0.99	...	...	...	...	3.10 $\pm$ 0.80

NOTE.—This table shows that CH<sub>3</sub>OH column densities obtained in this paper are consistent with those in Paper I, which are our recommended values.

NOTE.—Uncertainties are statistical errors from the Gaussian fits.



**B. Additional information on laboratory data**

TABLE B.3

ICE COMPOSITION, BAND MAXIMUM POSITION (“PEAK POSITION”), FWHM AND BAND STRENGTH RELATIVE TO THE PURE ICE ( $A_{\text{rel.}}$ ), LISTED FOR A SET OF ICE MIXTURES UNDER INVESTIGATION.

Ice mixture					Molecule	Peak position		FWHM		$A_{\text{rel.}}$	Mode	
NH <sub>3</sub>	CH <sub>3</sub> OH	H <sub>2</sub> O	CO	CO <sub>2</sub>		cm <sup>-1</sup>	$\mu\text{m}$	cm <sup>-1</sup>	$\mu\text{m}$			
1	0	0	0	0	NH <sub>3</sub>	1070	9.341	66	0.577	1	$\nu_2$	umbrella
1	0	0.11	0	0	NH <sub>3</sub>	1076	9.291	70	0.605	1	$\nu_2$	umbrella
1	0	1	0	0	NH <sub>3</sub>	1100	9.091	77	0.637	1	$\nu_2$	umbrella
1	0	9	0	0	NH <sub>3</sub>	1118	8.947	62	0.496	0.7	$\nu_2$	umbrella
1	0	10	1	0	NH <sub>3</sub>	1124	8.897	53	0.420	0.7	$\nu_2$	umbrella
1	0	1	1	0	NH <sub>3</sub>	1094	9.144	75	0.627	1	$\nu_2$	umbrella
1	0	10	0	2	NH <sub>3</sub>	1122	8.916	57	0.453	0.8	$\nu_2$	umbrella
1	0	1	0	1	NH <sub>3</sub>	1098	9.108	82	0.681	0.9	$\nu_2$	umbrella
1	0	0	1	1	NH <sub>3</sub>	1062	9.414	66	0.586	0.8	$\nu_2$	umbrella
1	4	0	0	0	NH <sub>3</sub>	1129 <sup>a</sup>	8.856 <sup>a</sup>	108 <sup>a</sup>	0.849	0.4 <sup>a</sup>	$\nu_2$	umbrella
1	4	0	0	0	CH <sub>3</sub> OH	1029	9.722	30	0.283	–	$\nu_4$	C-O stretch
1	4	0	0	0	CH <sub>3</sub> OH	1128	9.707	35	0.275	–	$\nu_7$	CH <sub>3</sub> rock
1	4	0	0	0	CH <sub>3</sub> OH	2823	3.543	28	0.035	–	$\nu_2$	C-H stretch
1	2	0	0	0	NH <sub>3</sub>	1111 <sup>a</sup>	8.994 <sup>a</sup>	115 <sup>a</sup>	0.934	0.6 <sup>a</sup>	$\nu_2$	umbrella
1	2	0	0	0	CH <sub>3</sub> OH	1029	9.720	29	0.274	–	$\nu_4$	C-O stretch
1	2	0	0	0	CH <sub>3</sub> OH	1132	8.833	35	0.273	–	$\nu_7$	CH <sub>3</sub> rock
1	2	0	0	0	CH <sub>3</sub> OH	2820	3.546	26	0.033	–	$\nu_2$	C-H stretch
1	1	0	0	0	NH <sub>3</sub>	1086	9.209	137	1.166	0.8	$\nu_2$	umbrella
1	1	0	0	0	CH <sub>3</sub> OH	1029	9.716	26	0.246	–	$\nu_4$	C-O stretch
1	1	0	0	0	CH <sub>3</sub> OH	1135	8.813	44	0.342	–	$\nu_7$	CH <sub>3</sub> rock
1	1	0	0	0	CH <sub>3</sub> OH	2817	3.550	26	0.033	–	$\nu_2$	C-H stretch
1	0.5	0	0	0	NH <sub>3</sub>	1080	9.258	118	1.015	0.8	$\nu_2$	umbrella
1	0.5	0	0	0	CH <sub>3</sub> OH	1030	9.711	22	0.207	–	$\nu_4$	C-O stretch
1	0.5	0	0	0	CH <sub>3</sub> OH	1128 <sup>a</sup>	8.865 <sup>a</sup>	35 <sup>a</sup>	0.275	–	$\nu_7$	CH <sub>3</sub> rock
1	0.5	0	0	0	CH <sub>3</sub> OH	2813	3.555	27	0.034	–	$\nu_2$	C-H stretch
1	0.25	0	0	0	NH <sub>3</sub>	1078	9.278	98	0.845	0.9	$\nu_2$	umbrella
1	0.25	0	0	0	CH <sub>3</sub> OH	1030	9.707	16	0.151	–	$\nu_4$	C-O stretch
1	0.25	0	0	0	CH <sub>3</sub> OH	– <sup>a</sup>	– <sup>a</sup>	– <sup>a</sup>	–	–	$\nu_7$	CH <sub>3</sub> rock
1	0.25	0	0	0	CH <sub>3</sub> OH	2808 <sup>a</sup>	3.561 <sup>a</sup>	17 <sup>a</sup>	0.022	– <sup>a</sup>	$\nu_2$	C-H stretch
1	1	1	0	0	NH <sub>3</sub>	1116 <sup>a</sup>	8.961	95	0.764	0.7	$\nu_2$	umbrella
1	1	1	0	0	CH <sub>3</sub> OH	1026	9.745	29	0.276	–	$\nu_4$	C-O stretch
1	1	1	0	0	CH <sub>3</sub> OH	1125 <sup>a</sup>	8.888 <sup>a</sup>	32 <sup>a</sup>	0.253	–	$\nu_7$	CH <sub>3</sub> rock
1	1	1	0	0	CH <sub>3</sub> OH	2824	3.541	26	0.033	–	$\nu_2$	C-H stretch
1	0.25	10	0	0	NH <sub>3</sub>	1119	8.937	59	0.472	1	$\nu_2$	umbrella
1	0.25	10	0	0	CH <sub>3</sub> OH	1017	9.833	22	0.213	–	$\nu_4$	C-O stretch
1	0.25	10	0	0	CH <sub>3</sub> OH	– <sup>a</sup>	– <sup>a</sup>	– <sup>a</sup>	–	–	$\nu_7$	CH <sub>3</sub> rock
1	0.25	10	0	0	CH <sub>3</sub> OH	2829 <sup>a</sup>	3.534 <sup>a</sup>	30 <sup>a</sup>	0.037	–	$\nu_2$	C-H stretch
1	1	10	0	0	NH <sub>3</sub>	1123	8.903	61	0.484	1	$\nu_2$	umbrella
1	1	10	0	0	CH <sub>3</sub> OH	1022	9.784	24	0.230	–	$\nu_4$	C-O stretch
1	1	10	0	0	CH <sub>3</sub> OH	– <sup>a</sup>	– <sup>a</sup>	– <sup>a</sup>	–	–	$\nu_7$	CH <sub>3</sub> rock
1	1	10	0	0	CH <sub>3</sub> OH	2830	3.533	15	0.019	–	$\nu_2$	C-H stretch
1	4	10	0	0	NH <sub>3</sub>	1130	8.848	62	0.489	–	$\nu_2$	umbrella
1	4	10	0	0	CH <sub>3</sub> OH	1023	9.777	30	0.288	–	$\nu_4$	C-O stretch
1	4	10	0	0	CH <sub>3</sub> OH	1124	8.896	23	0.183	–	$\nu_7$	CH <sub>3</sub> rock
1	4	10	0	0	CH <sub>3</sub> OH	2830	3.534	14	0.017	–	$\nu_2$	C-H stretch
0	1	0	0	0	CH <sub>3</sub> OH	1028	9.729	28	0.265	1	$\nu_4$	C-O stretch
0	1	0	0	0	CH <sub>3</sub> OH	1125	8.888	34	0.269	1	$\nu_7$	CH <sub>3</sub> rock
0	1	0	0	0	CH <sub>3</sub> OH	2828	3.536	33	0.041	1	$\nu_2$	C-H stretch
0	1	1	0	0	CH <sub>3</sub> OH	1025	9.755	33	0.314	–	$\nu_4$	C-O stretch
0	1	1	0	0	CH <sub>3</sub> OH	1124	8.897	40	0.317	–	$\nu_7$	CH <sub>3</sub> rock
0	1	1	0	0	CH <sub>3</sub> OH	2828	3.536	23	0.029	–	$\nu_2$	C-H stretch
0	1	9	0	0	CH <sub>3</sub> OH	1020	9.801	23	0.221	–	$\nu_4$	C-O stretch
0	1	9	0	0	CH <sub>3</sub> OH	1126	8.883	13	0.103	–	$\nu_7$	CH <sub>3</sub> rock
0	1	9	0	0	CH <sub>3</sub> OH	2828	3.536	23	0.029	–	$\nu_2$	C-H stretch
0	1	0	9	0	CH <sub>3</sub> OH	1034	9.675	25	0.229	–	$\nu_4$	C-O stretch
0	1	0	9	0	CH <sub>3</sub> OH	1119	8.938	30	0.242	–	$\nu_7$	CH <sub>3</sub> rock
0	1	0	9	0	CH <sub>3</sub> OH	2831	3.532	–	–	–	$\nu_2$	C-H stretch
0	1	0	9	0	CO	2138	4.677	7	0.014	–	$\nu_1$	C-O stretch

TABLE B.3—*Continued*

Ice mixture					Molecule	Peak position		FWHM		$A_{\text{rel.}}$	Mode	
NH <sub>3</sub>	CH <sub>3</sub> OH	H <sub>2</sub> O	CO	CO <sub>2</sub>		cm <sup>−1</sup>	μm	cm <sup>−1</sup>	μm			
0	1	0	1	0	CH <sub>3</sub> OH	1029	9.720	30	0.286	—	$\nu_4$	C-O stretch
0	1	0	1	0	CH <sub>3</sub> OH	1124	8.898	32	0.258	—	$\nu_7$	CH <sub>3</sub> rock
0	1	0	1	0	CH <sub>3</sub> OH	2830	3.534	—	—	—	$\nu_2$	C-H stretch
0	1	0	1	0	CO	2136	4.682	9	0.020	—	$\nu_1$	C-O stretch
0	9	0	1	0	CH <sub>3</sub> OH	1028	9.730	28	0.261	—	$\nu_4$	C-O stretch
0	9	0	1	0	CH <sub>3</sub> OH	1125	8.890	32	0.255	—	$\nu_7$	CH <sub>3</sub> rock
0	9	0	1	0	CH <sub>3</sub> OH	2824	3.541	—	—	—	$\nu_2$	C-H stretch
0	9	0	1	0	CO	2135	4.685	9	0.021	—	$\nu_1$	C-O stretch

<sup>a</sup>Band is weak and spectral overlap prohibits accurate fitting.

### C. Comparison between astronomical and laboratory data for all sources

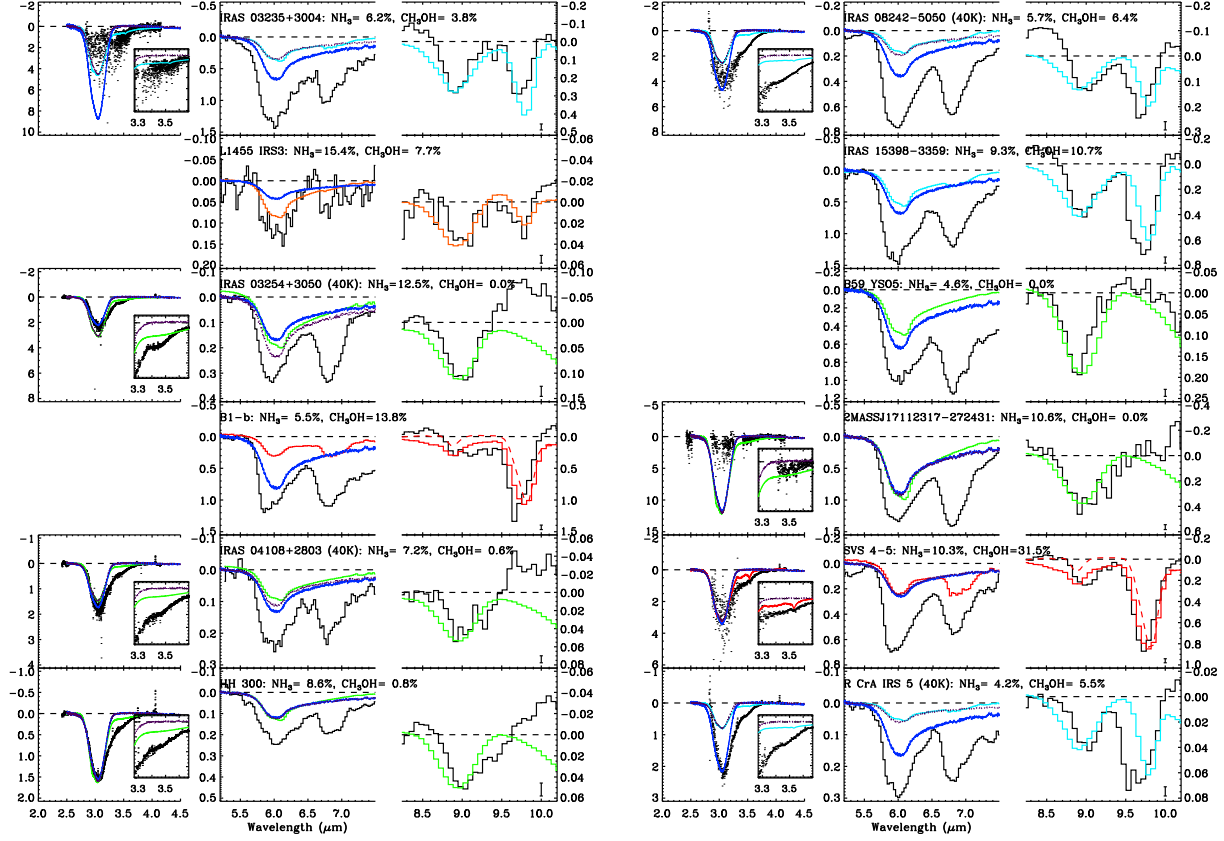


Fig. C.1.— (a) Comparison between astronomical and laboratory data for sources whose silicate absorption feature was fitted with a template. For a given source (displayed in either the left or right column of the figure), the middle and right panels show 5.2-7.5 and 8.2-10.2  $\mu\text{m}$  regions from IRS *Spitzer* spectra overlaid with laboratory spectra, scaled to the 9- $\mu\text{m}$   $\text{NH}_3$  umbrella mode, and smoothed to the *Spitzer* resolution. Error bars for the *Spitzer* spectra are indicated in the bottom-right corner. The dark blue line represents the pure water laboratory spectrum scaled to the water column density taken in paper I. Other colors are representative of laboratory spectra obtained for the following mixtures:  $\text{H}_2\text{O}:\text{NH}_3=9:1$  (green),  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3=10:0.25:1$  (orange),  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3=10:1:1$  (cyan), and  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3=10:4:1$  (red). When available (see Boogert et al. 2008), VLT or Keck data (2.0-4.5  $\mu\text{m}$ , left panel) are also plotted. In this case, we overplotted (dotted purple line) a pure water spectrum scaled to the 3- $\mu\text{m}$  water feature of the mixed ice spectrum. Whenever present, a red dashed line in the right panel of a given source represents a  $\text{H}_2\text{O}:\text{CH}_3\text{OH}=9:1$  laboratory spectrum scaled to the 9.7- $\mu\text{m}$   $\text{CH}_3\text{OH}$  CO-stretch mode: this gives an indication of the contribution of the 9- $\mu\text{m}$   $\text{CH}_3\text{OH}$   $\text{CH}_3$ -rock mode to the total 9- $\mu\text{m}$  feature. The laboratory spectra are recorded at 15 K unless indicated differently.

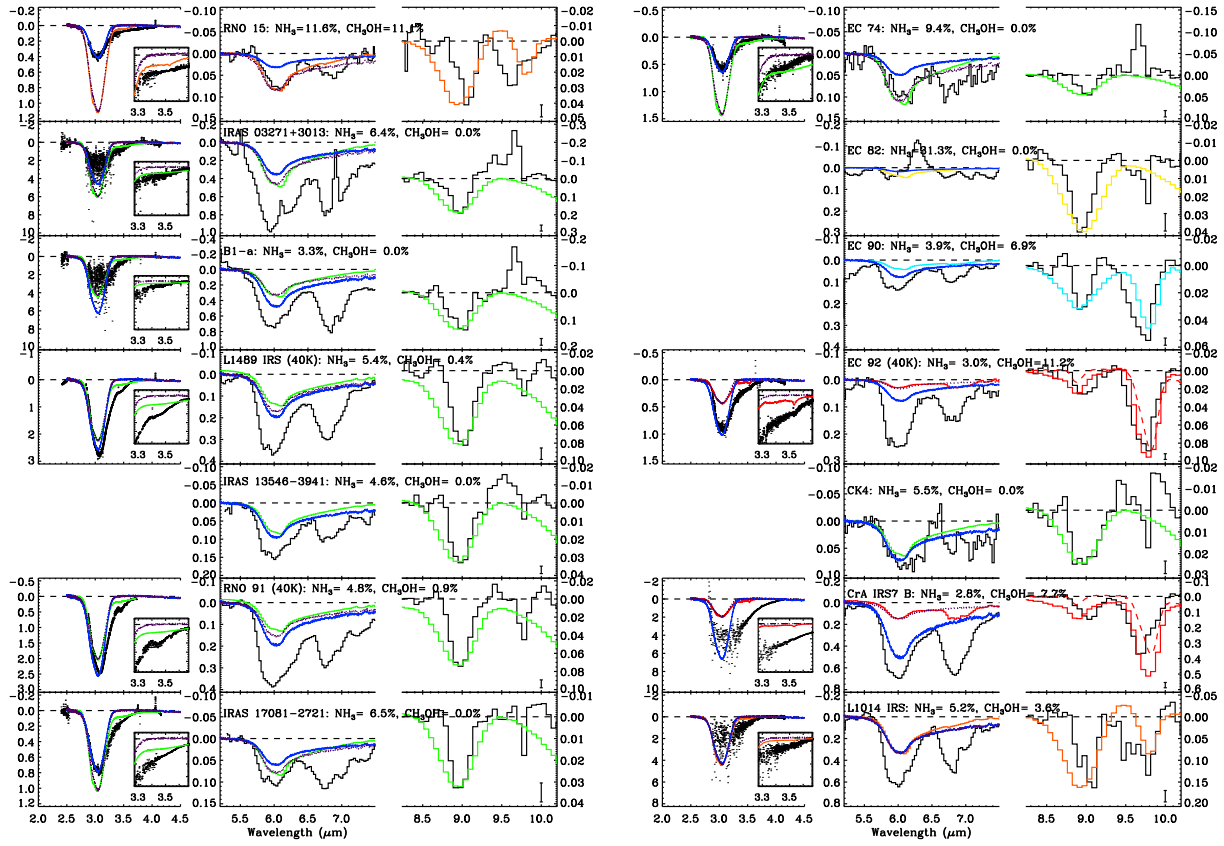


Fig. C.1.— (b) As (a) but for sources with no associated template, i.e. with the 10- $\mu$ m silicate feature subtracted via the local continuum method. Additionally, yellow represents  $\text{H}_2\text{O}:\text{NH}_3=4:1$  (H. Frazer, priv. comm.).

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